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TABLE OF CONTENTS

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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR
DIVISION OF CHEMICAL SCIENCES

1955, No. 6

NOVEMBER - DECEMBER

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SALUTATION TO ALEKSANDR NAUMOVICH FRUMKIN

on the Occasion of his Sixtieth Birthday

The Division of Chemical Sciences of the Academy of Sciences of the USSR and the Editorial Board of the Bulletin of the Academy of Sciences, Division of Chemical Sciences congratulate you on the occasion of your sixtieth birthday and of the completion of forty years of scientific activity.

Your many and varied physicochemical investigations— particularly in the field of electrochemistry —form a very significant contribution to science.

We hope that you will enjoy good health and will continue in your successful creative work.

DIVISION OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U S S R.

EDITORIAL BOARD OF THE BULLETIN OF THE ACADEMY OF SCIENCES OF THE U S S R,

DIVISION OF CHEMICAL SCIENCES

EFFECT OF THE METHOD OF MAKING MODIFYING ADDITIONS ON THE PROPERTIES
OF OXIDE CATALYSTS

G. M. Zhabrova and E. A. Fokina

The way in which additives are distributed at the surface and in the body of a catalyst and the possibility of interaction between additives and the catalyst are matters of great interest for the understanding of the laws governing the action of additives on catalysts. It was considered probable that change in the method of introducing additives can result in a change in their distribution in the catalyst and have a substantial effect on the catalytic properties of the catalyst.

As a model reaction of the oxidation-reduction type we made use of the decomposition of hydrogen peroxide in presence of magnesium oxide [1]. It was found that, in the pure state, magnesium oxide has only moderate catalytic activity, and this facilitated the detection of positive effects attributable to additions. Stannic oxide was selected as additive; in the pure state this substance has a negligible catalytic effect. The rate of decomposition of hydrogen peroxide was determined gasometrically, the procedure being similar to that described previously [1].
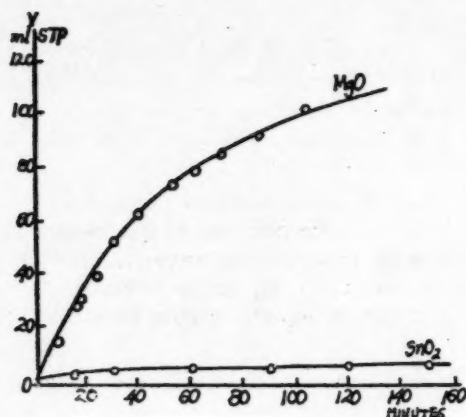
Fig. 1. Kinetic curves for the decomposition of hydrogen peroxide over magnesium oxide and over stannic oxide (reaction temperature 45°)

Fig. 1 shows kinetic curves for the decomposition of hydrogen peroxide over pure magnesium oxide and over pure stannic oxide. It will be seen that the activity of the former is about 35-40 times as great as that of the latter. As stannic oxide is introduced into the magnesium oxide in small amounts (0.01-6.4%), the effect of the simple summation of the activities of the two oxides can be neglected.

For the introduction of stannic oxide into magnesium oxide, the following three methods were used:

1. Impregnation of prepared magnesium oxide with solutions of tetraphenyltin. Magnesium oxide is impregnated with chloroform solutions of tetraphenyltin at various concentrations, dried at 100-120°, and calcined for one hour at 600° in a quartz vessel in an atmosphere of air. Pyrolysis of tetraphenyltin gives phenyl radicals and atomic tin, which is oxidized by atmospheric oxygen to stannic oxide (Series 1).

2. Impregnation of prepared magnesium oxide with solutions of stannic chloride. Magnesium oxide is impregnated with aqueous stannic chloride solutions of various concentrations, and the stoichiometric amount of 20% sodium carbonate solution is added to the resulting paste. The catalyst samples prepared in this way are washed, dried, and calcined for four hours at 450° in a quartz vessel in an atmosphere of air (Series 2).

3. Coprecipitation of magnesium and tin salts with sodium carbonate solution, the basic carbonates formed being washed, dried, and calcined at 450° (Series 3).

The amount of stannic oxide introduced was determined by polarography and spectrum analysis.

For our study of the catalytic properties of the magnesium oxide samples containing additions of stannic oxide it was necessary to select a method of determining the relative activities of the samples. It was established that the course of the decomposition of hydrogen peroxide is satisfactorily described by a first-order equation. The value of

the rate constant served as a measure of the activity of the catalyst. Rate constants could be determined accurate within 5 %.
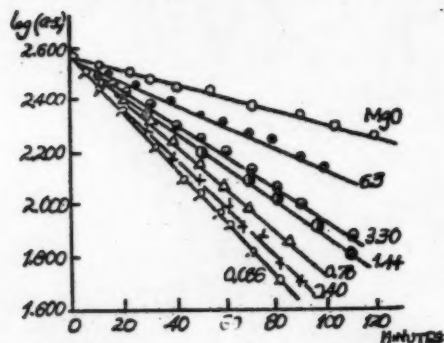
Fig. 2. Kinetic curves for the decomposition of hydrogen peroxide plotted in accordance with the first-order law for the samples of Series 1. The decomposition reaction was carried out at 90°. The figures on the curves denote stannic oxide contents (%)

Fig. 3a. Dependence of the activity of catalyst samples of Series 1 on stannic oxide content. The figures on the curves denote reaction tempertures

It is interesting that increase in stannic oxide content form 0.046 to 6.3% by weight did not alter the form of the kinetic law (a first-order equation), but affected only the value of the rate constant. This can be seen from the linear form of the curves in Fig. 2, which express the dependence of the logarithm of the amount of unchanged hydrogen peroxide on time.

Fig. 3b. Dependence of the specific activity of the same samples on stannic oxide content.

Our study of the dependence of catalyst activity on stannic oxide content showed that the form of this relationship varies with the temperature of the reaction. This is illustrated in Fig. 3a for reaction temperatures ranging from 20° to 90°. Thus, at 90° there is a maximum at an additive content of 0.086%, and at this point the activity is 4.1 times as great as that of pure magnesium oxide. At 75° there is a maximum at the same stannic oxide content, but the effect of the addition is somewhat less than at 90°.

When the reaction temperature is lowered further to 45°, the maximum moves from 0.086% to 0.40%, and the activity relative to that of pure magnesium oxide is 2.1. Finally, at still lower temperatures (20° and 5°), the maximum disappears, and, beginning from the very smallest amounts of additive, the activity is less than that of pure magnesium oxide. As the temperature of the catalytic reaction is lowered, the curves for the dependence of the specific activity of the catalyst on additive content flatten out (Fig. 3b).

This behavior indicates that the value of the activation energy varies for the different catalyst samples (pure magnesium oxide and magnesium oxide containing stannic oxide). A summary of data on the activation energy and pre-exponential factor is given in Table 1. The probable error in the determination of activation energy is ±0.5 kcal / mole.

It follows from the data in Table 1 that a substantial change in the activation energy and in the logarithm of the pre-exponential factor is brought about by the first very small additions of stannic oxide. In the further range of additions from 0.40 to 3.30, the variations in activation energy and in the logarithm of the pre-exponential factor are approximately equal to the experimental error. At high stannic oxide contents both quantities are reduced somewhat.

TABLE 1

Dependence of the Activation Energy and the Logarithm of the Pre-exponential Factor on the Stannic Oxide Content of a Magnesium Oxide Catalyst (Series 1)

SnO_2 content (%)	E (kcal/mole)	$\log K_0$
None	13.0	6.6
0.046	17.5	9.7
0.086	18.0	10.2
0.095	17.5	9.7
0.40	17.5	9.6
0.78	17.0	9.5
1.20	17.5	9.6
1.44	17.0	9.4
3.30	17.0	9.4
6.30	16.5	9.0

The values of the pre-exponential factor vary symbatically with the values of the activation energy. It should be noted that a symbatic relationship between E and $\log K_0$ as the content of additives in oxide catalysts is increased was observed by Todes and Margolis [2] and by Margolis and Krylov [3] for the high-temperature oxidation of isooctane. The more marked dependence of catalyst activity on stannic oxide content at higher temperatures gives reason to suppose that stannic oxide is a modifying additive [4, 5].
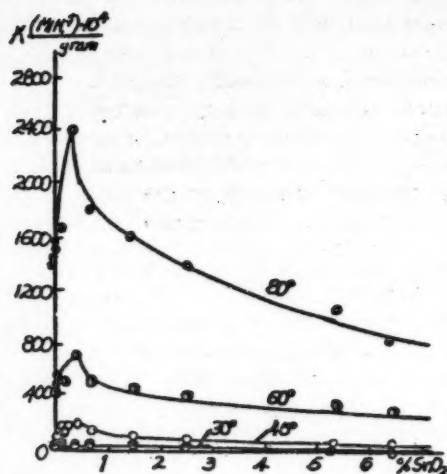
Fig. 4a. Dependence of the activity of catalyst samples of Series 2 on stannic oxide content (at various reaction temperatures).
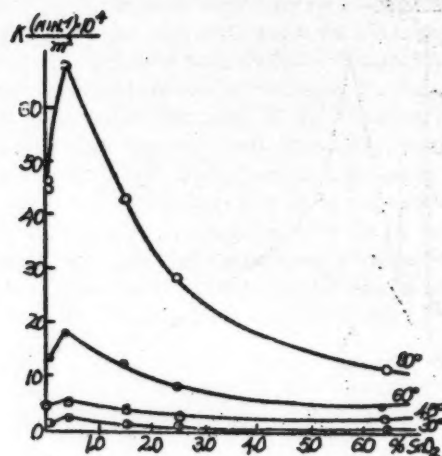
Fig. 4b. Dependence of the specific activity of the same samples on stannic oxide content

Similar regularities, though not so marked, are to be observed for the preparations of Series 2. For the maximum point (0.4% SnO_2) at 80°, the activity of the modified catalyst is 1.7 times as great as that of pure magnesium oxide. As the temperature is lowered, this ratio diminishes (Fig. 4a). As in the previous case, the observed variation in the form of the curve for catalytic activity against additive content is to be attributed to the variation in the values of the activation energy and pre-exponential factor for reactions over the catalyst samples (pure magnesium oxide and magnesium oxide with various additions of stannic oxide). The range of variation is somewhat less here than in Series 1: the activation energy varies from 14.0 to 16.5 kcal/mole, and the logarithm of the pre-exponential factor from 7.7 to 9.8. Hence, similar regularities are found both when the introduction of stannic oxide into prepared magnesium oxide is made originally in the form of an organic tin compound, and when it is intorduced as an inorganic tin compound.

The behavior found when the catalyst is prepared by the coprecipitation of magnesium and tin salts (Series 3) differs greatly from that found in Series 1 and 2, in which the additive was formed on the prepared catalyst, the curve for catalytic activity against additive content now having a minimum corresponding to a content of 0.02% SnO_2 and a maximum corresponding to 1.0% SnO_2 (Fig. 5). The increase in activity at the maximum point (as compared with the activity of the pure oxide) is only slight, the ratio of constants being 1.3 at 80°. It should be noted that the form of the curve for rate constant against content of modifying addition (Fig. 5) is similar to that of the curve for the rate constant of hydrogen peroxide decomposition at platinized platinum treated with a catalytic poison (arsenious oxide), as determined by Shlygin [6]. Element [7], who investigated the effect of additions of aluminum oxide and nitric acid to nickel oxide in oxidation reactions, also observed a complicated relationship between catalytic activity and additive content, there being a minimum and a maximum catalytic activity.

Returning now to the consideration of our results, we must point out that for this series of catalysts the activation energy and pre-exponential factor again vary within very narrow limits with variation in the amount of additive introduced. Thus, for pure magnesium oxide, and also for magnesium oxide containing 6% of stannic oxide, the activation energy is 14.0 kcal/mole, whereas for magnesium oxide containing 1% of stannic oxide — E = 16.0 kcal//mole.

In order to obtain a more accurate picture of the action of the modifying addition and the dependence of its effect on the method by which it is introduced, the study of the catalytic properties of the samples was supplemented by an examination of their adsorptive properties (form of the nitrogen and heptane adsorption isotherms, their specific surfaces, etc.). It was then shown [8] that the introduction of stannic oxide onto prepared magnesium oxide (Series 1 and 2) leads to a marked increase in specific surface, whereas introduction of the same additive into magnesium oxide by the coprecipitation method (Series 3) has almost no effect on the specific surface of the catalyst.

Fig. 6 shows the dependence of the specific surfaces of catalysts of the three series on the stannic oxide contents. It will be seen that the introduction of small amounts of stannic oxide results in a considerable increase in the specific surface of the catalyst (this effect is particularly marked for samples of Series 1), and the introduction of 6.3% of stannic oxide produces a fourfold increase in specific surface in samples of Series 1 and a twofold increase in samples of Series 2.

It is quite impossible to explain this increase by the simple summation of the specific surfaces of catalyst and additive, for nitrogen-adsorption experiments on samples of pure magnesium oxide catalyst, of magnesium oxide catalyst containing 6.4% of stannic oxide, and of a mechanical mixture of magnesium oxide and 6.4% of stannic oxide showed that the adsorption isotherm of the mixture is close to that of pure magnesium oxide (Fig. 7). It may be noted also that, as indicated by an elementary calculation, for simple summation to be possible it must be assumed that the stannic oxide introduced has a physically unreal specific surface (more than 1000 sq.m/g). All these considerations, supported also by results from measurements of the pore structures of the catalysts, led us to the conclusion

Fig. 5. Dependence of the activity of magnesium oxide catalysts of Series 3 on stannic oxide content (at various reaction temperatures)

[8] that the introduction of stannic oxide by the impregnation of prepared magnesium oxide probably results in the formation of a surface compound of tin and magnesium oxides and the breaking-up of the magnesium oxide surface. On the other hand, the introduction of stannic oxide into magnesium oxide by the coprecipitation method results in the preferential distribution of the additive within the micrograins of the catalyst.

Fig. 8 represents the dependence of specific activity (expressed as the unimolecular rate constant for the decomposition of hydrogen peroxide divided by the specific surface of the catalyst) on the stannic oxide content of the magnesium oxide catalyst. The same figure shows also the dependence of the specific surface of the catalyst on the stannic oxide content, which is expressed by a curve that rises steeply at first and then passes over into a more gently

rising portion. The region of the transition from the sharp rise to the gentle slope corresponds closely to the region of optimum catalytic activity on the modification curve. This behavior gives rise to the hypothesis of a change in the chemical composition of the catalyst surface in the region of optimum catalytic activity, probably associated with the formation of a special kind of surface compound between stannic oxide and magnesium oxide (possibly a type of stannate) which breaks up the magnesium oxide surface. It is evident that, as the stannic oxide content of the magnesium oxide catalyst is increased, separate patches of finely dispersed stannic oxide are formed on the surface, with the result that partial blocking of the surface occurs. This change in the catalyst surface corresponds to the gently sloping part of the curve for the change in specific surface, and it is accompanied by a fall in catalytic activity. It may be supposed that with further increase in the stannic oxide content a more complete blocking of the magnesium oxide surface occurs as a result of the formation of a layer of finely dispersed stannic oxide. As the catalytic activity of stannic oxide is very much less than that of magnesium oxide, this blocking must result in very much reduced catalytic activity in magnesium oxide samples having a high stannic oxide content, and our observations on a catalyst sample having a 20% stannic oxide content confirm this. It should be noted that only at stannic oxide contents of 3% and greater do the lines of stannic oxide appear in the X-ray diffraction pictures of the samples (Series 1 and 2).
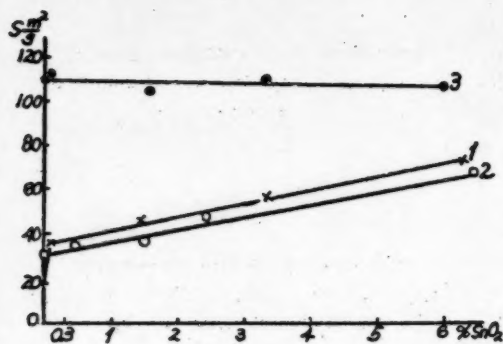
Fig. 6. Dependence of the specific surface of the catalyst (determined by the adsorption of heptane) on the content of stannic oxide introducted by different methods).

A different picture is observed when the addition of stannic oxide is made by the coprecipitation method. The lack of dependence of specific surface on stannic oxide content gives reason to suppose that the stannic oxide is mainly within the micrograins of the catalyst and only a very small portion of it is on the catalyst surface. Accordingly, the stannic oxide content at the maximum point (1%) is much greater than at the maxima of the modification curves of catalyst samples of Series 1 and 2 (0.086% and 0.4%). It is evident that, in the present case, no finely dispersed film of stannic oxide is formed on the catalyst surface at higher stannic oxide contents; X-ray diffraction pictures support this view, weak SnO_2 lines being found only in samples containing 6.0% or more of stannic oxide. It must be supposed that here again magnesium stannate is formed and occurs, together with stannic oxide, within the micrograins of the catalyst. However, it is clear that we are dealing with a complex case of modification which deserves more detailed study.

Our results enable us to infer that in the catalytic system investigated the method of introducing the additive has an important effect on the properties of the catalyst and on the way in which the additive acts. The method of introducing the additive by treatment of the prepared catalyst — which we effected by impregnation of magnesium oxide with organic and inorganic tin compounds and subsequent pyrolysis — apparently leads to the formation of surface compounds between the catalyst and the additive, to the breaking-up of the surface, and to the modification of the catalyst. Considered in relation to the classification of catalyst additives proposed by Roginsky [4], stannic oxide, introduced by this method, may be considered to be both a modifying and a structure-forming additive.

The coprecipitation method contrasts sharply with the above-mentioned methods and results in quite a different distribution of stannic oxide in the magnesium oxide (essentially within the micrograins of the catalyst). The way in which the additive acts is also quite different, the dependence of catalyst activity on stannic oxide content being represented by a complex curve having a maximum and a minimum.

In conclusion it must be pointed out that most investigators have assumed that the chemical composition of the catalyst and additive unequivocally determines the manner in which the catalytic system acts. From the data provided by the present investigation it will be clear that for a given additive content in the catalyst the action of the catalyst, and also, probably, the additive concentration at the catalyst surface, may vary greatly according to the method used for introducing the additive. It is probable that catalysis and adsorption effects attributable to the method of introducing additives are not limited to the particular system that we have studied, but constitute a factor that must be taken into account in other catalytic systems.
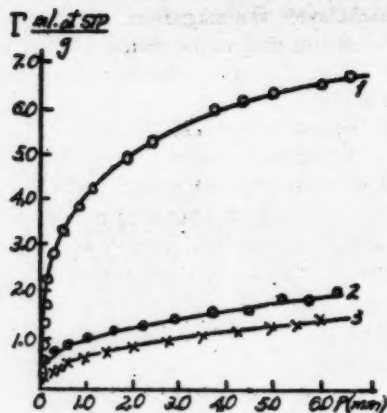
Fig. 7. Isotherms for the adsorption of nitrogen at −183°; 1 - sample of magnesium oxide catalyst containing 6.4% of stannic oxide (Series 2); 2 - mixture of magnesium oxide with 6.0% of stannic oxide; 3 - pure magnesium oxide
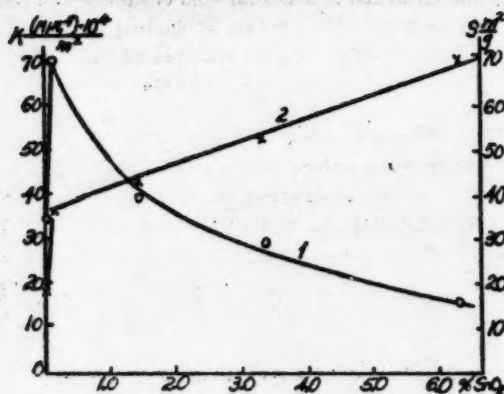
Fig. 8. Dependence of the specific activity (1) and the specific surface (2) of magnesium oxide samples of Series 1 on stannic oxide content

SUMMARY

1. A study was made of the catalytic and adsorptive properties of magnesium oxide samples containing additions of stannic oxide introduced in quantities of 0.01-6.4% by various methods: by application to prepared magnesium oxide via organic and inorganic tin compounds, and by coprecipitation.

2. It was shown that the introduction of stannic oxide into magnesium oxide by impregnation with tetraphenyl tin or stannic chloride results in a modification of the action of the magnesium oxide catalyst in the decomposition of hydrogen peroxide. The main effect is already brought about by the very smallest additions of stannic oxide. As the temperature of the catalytic process is lowered from 90° to 5°, the modification curves change in form, becoming flattened out.

3. The dependence on stannic oxide content of the activity of catalysts prepared by the coprecipitation of magnesium and tin salts is expressed by a curve having a minimum and a maximum. Minimum catalytic activity corresponds to a stannic oxide content of 0.02% and maximum activity to a stannic oxide content of 1%.

4. Change in the method of introducing the additive not only affects the catalytic properties, but also — as we showed previously—results in a marked change in the adsorptive properties of the catalyst. When stannic oxide is introduced into prepared magnesium oxide, the adsorptivity and specific surface of the sample increases with increase in additive content. When stannic oxide is introduced into magnesium oxide by coprecipitation, the adsorptivity and specific surface of the products are almost unaffected by increase in additive content.

5. On the basis of a comparison of the catalytic and adsorptive properties of the catalysts studied, we have advanced the hypothesis that the ways in which additions of stannic oxide are incorporated into magnesium oxide are of two different types and that the manner in which the additions act depends on the method by which they are introduced into the catalyst.

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SOLID SOLUTIONS OF CALCIUM ALUMINOFERRITES

N. A. Toropov and A. I. Boikova

Solid solutions of calcium aluminoferrites are formed in the ternary system $CaO - Al_2O_3 - Fe_2O_3$ by mutual solution of $2CaO \cdot Fe_2O_3$ and $5CaO \cdot 3Al_2O_3$ (and probably a small amount of calcium oxide).

The first investigators of the system $CaO - Al_2O_3 - Fe_2O_3$, Hansen, Brownmiller, and Bogue [1], established the existence of only one ternary compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in the region of high calcium oxide contents. Tetracalcium aluminoferrite has high refractive indices $Ng = 2.08_{(Na)}$ and $N_p = 1.96_{(Na)}$, and it is pleochroic in dark to light brown tones. $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and compounds whose fields of stability border on that of the aluminoferrite in the ternary system, namely, $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, CaO, are important components of clinker. It is obvious that the system as a whole, and especially those parts bordering on the field of calcium oxide, is of considerable interest for the study of the structure of cement clinker. Particular attention has been turned on the investigation of ferrites and aluminoferrites. This interest has been aroused under the following circumstances. Lea and Parker [2] and Guttman and Gille [3], in investigations on synthetic calcium aluminoferrites and on the aluminoferrites of industrial clinkers, obtained crystals of these substances having lower refractive indices than $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. This could result by the dissolution in the aluminoferrites of compounds of lower refractive index, i.e. aluminates. Another very important fact confirmed the correctness of this last supposition. Investigation of the clinkers by crystal optics indicated a noncorrespondence between the actually observed and calculated (on the basis of chemical analysis) amounts of calcium aluminates. The calculated amount of aluminates was always greater than the actual amount.

One of the first investigations on solid solutions of calcium aluminoferrites was that of Toropov, Merkov, and Shishakov [4] on the binary system $5CaO \cdot 3Al_2O_3 - 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The system was studied by crystal optics and by X-ray methods. The formation of solid solutions was confirmed by the continuous lowering of the refractive indices of the aluminoferrites. The authors established that the maximum amount of $5CaO \cdot 3Al_2O_3$, dissolved by $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is 35% by weight. The formula of the calcium aluminoferrite consisting of 35% by weight of $5CaO \cdot 3Al_2O_3$ and 65% by weight of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is $43CaO \cdot 16Al_2O_3 \cdot 7Fe_2O_3$. Whereas the ferric oxide content of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is 32.8% by weight, that of this aluminoferrite is 21.7% by weight. Calcium aluminoferrite of this composition has refractive indices of $N_g = 1.93$, $N_p = 1.87$. The authors confirmed the existence of solid solutions by X-ray diffraction.

Almost simultaneously with this work indications of solid solutions between $5CaO \cdot 3Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ were obtained by McMurdie [5], who concluded that $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ can dissolve only 5% by weight of $5CaO \cdot 3Al_2O_3$. However, according to Jamauchi [6], a homogeneous solid solution of composition $6.2CaO \cdot 2.2Al_2O_3 \cdot Fe_2O_3$ (21.8% by weight of ferric oxide) can exist. Newman [7] determined heats of solution for a series of solid solutions of aluminoferrites, and he showed that they depend linearly on composition.

The results of Toropov, Merkov, and Shishakov [4] have been criticized on several occasions -- right up to 1946, infact, when Swayze [8] confirmed their correctness. According to Swayze's results, a continuous series of solid solutions extends as far as the composition $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ (22.8% by weight of ferric oxide), or $42CaO \cdot 14Al_2O_3 \cdot 7Fe_2O_3$. When this formula is compared with $43CaO \cdot 16Al_2O_3 \cdot 7Fe_2O_3$, the formula given by the authors of the 1937 work, no great discrepancy is to be found. Moreover, the latter formula is appreciably closer in composition to the aluminoferrite having the maximum content of aluminate in solid solution (the so-called limiting solid solution). Actually, according to Swayze the limiting solid solution contains 22.9% by weight of ferric oxide, and according to Toropov, Merkov, and Shishakov it contains 21.7% by weight.

Hence, the composition proposed by Swayze for the final member of the series of solid solutions is only a rough approximation to the limiting composition of solid solutions. This is still more obvious when we consider the work of Italian investigators. Thus, Malquori [9] and Cirilli and Burdese [10], in X-ray studies of solid solutions of aluminoferrites, concluded that a homogeneous solid solution can be obtained having a ferric oxide content of 20-21%. Malquori [9] suggested that the formula of the aluminoferrite of maximum aluminate content is $6CaO \cdot 2.1Al_2O_3 \cdot 0.9Fe_2O_3$ (20.7% by weight of ferric oxide).

The originality of the procedure used by Cirilli and Brisi [11] for the investigation of aluminoferrites is worthy of note. They made use of the magnetic properties of aluminoferrites and measured their magnetic susceptibilities. They showed that the magnetic susceptibility of these substances increases as the alumina modulus increases and assumes a certain constant value from the point at which the molar ratio Al_2O_3/Fe_2O_3 attains the value of two. There is an inflection in the curve at the composition $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$. As regards the accuracy of this method, we do not consider it very high, inasmuch as the inflection occurs at a point at which the aluminoferrite contains 22.8% by weight of ferric oxide. The results that we have discussed indicate that the limiting composition of the solid solutions corresponds to less than this content of ferric oxide, so that the inflection should occur to the left of the composition of 22.8% by weight of ferric oxide. However, the procedure described is of interest in that it permits the composition of aluminoferrites to be determined approximately from their magnetic characteristics.

Summarizing the results of the investigations examined, we may make the following statements. Between calcium ferrites and aluminates a series of solid solutions aluminoferrites is formed. In general, these solutions are formed by the partial replacement of iron by aluminum in dicalcium ferrite. Complete replacement would lead to dicalcium aluminate $2CaO \cdot Al_2O_3$, which does not exist as an individual chemical compound. Another aluminate — $5CaO \cdot 3Al_2O_3$ — appears on the phase diagram, and we consider that this substance forms solid solutions with calcium ferrite and a certain amount of calcium oxide. The compositions $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ should be regarded as intermediate members of this series of solid solutions.

EXPERIMENTAL

Selection of Method of Investigation. In view of the interest presented by this question, we set ourselves the tasks 1) of investigating solid solutions of aluminoferrites with the object of determining the composition corresponding to maximum saturation with aluminate; and 2) of determining whether aluminoferrites of variable composition are present in industrial clinkers.

We consider that, of all the above-mentioned methods for the investigation of solid solutions of aluminoferrites, the most accurate for these particular compositions is the method of crystal optics. It must be stated that few of the investigators of aluminoferrites have used this method. The sensitivity of one of the most accurate methods of investigation — the X-ray method — is low in the case of the aluminates and aluminoferrites with which we are concerned, and the contents of these in a mixture cannot be determined for less than the following values; $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ —15%, and aluminates ($5CaO \cdot 3Al_2O_3$ and $3CaO.Al_2O_3$)— 6% [12]. On the other hand, when the optical method of investigation is used, these minerals can undoubtedly be determined in such amounts or even in very much less amounts (1-2%), when the large differences in refractive index are taken into account. In studying solid solutions of aluminoferrites by the X-ray method, Malquori, Cirilli, and Burdese did not take these important facts into account. Apart from the selection of the method of investigation, it was necessary also for us to arrange the conditions of the experiment so that the melts could be cooled as slowly as possible; in this way favorable conditions can be created for the crystallization of aluminoferrites when determining the composition of the solid solution having the maximum aluminate content. We shall not discuss the experimental arrangement for the synthesis; the melts were cooled at the rate of 1.5° per minute.

a'-$5CaO \cdot 3Al_2O_3$ as a Component of the Solid Solution. In order the resolve the question of the modification of aluminate that dissolves in the ferrite and the maximum content of aluminate in solid solution, a study was made of a series of compositions along the line of solid solutions which starts from dicalcium ferrite. As regards the section $2CaO \cdot Fe_2O_3$ — $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, Hansen, Brownmiller, and Bogue [1] have already established that a continuous series of solid solutions is formed between the components. This was later confirmed by the X-ray investigations of Solacolu [13].

We consider that the aluminate component of solid solutions of aluminoferrites is not the hypothetical $2CaO \cdot Al_2O_3$, as some investigators suppose, but $5CaO \cdot 3Al_2O_3$.

Pentacalcium trialuminate exists in two modifications: a-$5CaO \cdot 3Al_2O_3$, (cubic syngony; N=1.608) and a'-$5CaO \cdot 3Al_2O_3$, (rhombic syngony; $N\tilde{g} = 1.692$, and $N_p = 1.687$.

The rhombic modification of $5CaO \cdot 3Al_2O_3$, which is known as "unstable $5CaO \cdot 3Al_2O_3$", has the space group $P_{2_1 2_1 2}$ or P_{mmm} [14].

A study of rotation X-ray diagrams and Weissenberg diagrams of monocrystals of $2CaO \cdot Fe_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ enabled us to establish the space group $V_h^{28}(I_{mma})$ for the compounds. $2CaO \cdot Fe_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ belong to the rhombic syngony. The space group of pentacalcium trialuminate P_{mmm} (or $R_{2_1 2_1 2}$ and the space group of dicalcium ferrite and of tetracalcium aluminoferrite I_{mma} belong to the rhombic syngony.

It was natural to suppose that the solid solution of aluminoferrites was formed with the participation not of the cubic form of $5CaO \cdot 3Al_2O_3$, as previously considered, but of the rhombic modification, which is structurally closer to $2CaO \cdot Fe_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. In order to verify this supposition, we calculated the theoretical curve (Table 1) and constructed graphs for the dependence of the refractive index of the aluminoferrite on the ammount of a- or a'-$5CaO \cdot 3Al_2O_3$ dissolved in it. In this calculation we assumed additivity, i.e. a linear relation between the composition of the solid solutions and refractive index. A relation of this kind is closely followed in many systems containing solid solutions. By way of example we may cite the series investigated by Bowen and Schairer [15]: $Mg_2SiO_4 - Fe_2SiO_4$, $MgO-FeO$, $MgSiO_3 - FeSiO_3$.

We then synthesized solid solutions for the field of compositions in which the preparations consist of a single phase — a solid solution containing not less than 20% of ferric oxide. The refractive indices of these solid solutions were measured, and the values were plotted on the same diagram. It was found that the experimental values of the refractive index correspond to the values calculated for a'-$5CaO \cdot 3Al_2O_3$ of rhombic syngony (figure). In the further work we calculated the compositions of aluminoferrites on the assumption that the solid solution was formed with participation of the rhombic modification of $5CaO \cdot 3Al_2O_3$.

For the immersion investigation of aluminoferrites we used phosphorus immersion liquids obtained from the Geological Institute of the USSR Academy of Sciences. These liquids contained methylene iodide, white phosphorus, and sulfur. The refractive indices were measured in sodium light.

Limiting Concentration of the Solid Solution. By the term "limited concentration of the solid solution" is to be understood, in this case, the pentacalcium trialuminate concentration in the aluminoferrite solid solution having a maximum content of this substance. In order to resolve the main question — what is the maximum content of $5CaO \cdot 3Al_2O_3$ in the solid solution and to what limit the amount of ferric oxide is accordingly reduced in the limiting aluminoferrite? — we synthesized and studied mixtures containing 42, 32, 24, 20, 16, 14 and 12 % by weight of ferric oxide. Table 2 shows the compositions of these mixtures.

Each sample was given four heat treatments: two sinterings and two fusions. The melts were cooled at 1.5° per minute. The samples were studied under the microscope by reflected and transmitted light. Samples containing more than 20% of ferric oxide consisted of homogeneous phases — solid solutions of aluminoferrites. Their grains showed pleochroism in light to dark brown tones. With increase in ferric oxide content the aluminoferrites became more and more intensely colored. Samples containing 16, 14, and 12% by weight of ferric oxide presented a different picture. In addition to aluminoferrite they contained also aluminates ($3CaO \cdot Al_2O_3$ and $5CaO \cdot 3Al_2O_3$), which are readily distinguished by reflected light (particularly after etching of the section with alcoholic oxalic acid) and when immersed. As the ferric oxide content of the samples increased from 14%, the refractive indices of the aluminoferrites present increased, but the aluminoferrites in the samples containing 14 and 12% of ferric oxide had identical refractive indices. This gave us reason to suppose that in these two samples the compositions of the aluminoferrites were identical. We therefore considered that the limiting composition of the solid solution (having the maximum aluminate content) had been reached.

Hence, the maximum lowering of the refractive index of the aluminoferrites is observed in samples containing 14 and 12% of ferric oxide. From the values $Ng = 2.08$ and $Np = 1.98$ for $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ we derived the values of $Ng = 1.914$ and $Np = 1 854$ (birefringence $- 0.06$) for the sample having the maximum content of aluminate in solid solution (limiting solid solution). The compositions of the aluminoferrites were calculated from these data.

Table 3 gives the results of the optical investigation of the synthetic aluminoferrites, their compositions expressed in weight and mole percentages, and their formulas. The composition of the aluminoferrite having the maximum content of pentacalcium trialuminate in solid solution is expressed by the formula $7.8CaC \cdot 3.24Al_2O_3 \cdot 1Fe_2O_3$. The limiting composition of the solid solution can be presented approximately in the form $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$, (17.5% by weight of ferric oxide). The amount of ferric oxide is 17.2% by weight.

Structure of Aluminoferrites. A very general idea of the structure of aluminoferrites can be gained from the structure of tetracalcium aluminoferrite, which was partially investigated by Büssem [16]. The elementary cell contains two $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ molecules and has the parameters $a_0 = 5.34$ A, $b_0 = 14.14$ A, $c_0 = 5.52$ A.

According to Büssem, the rhombic lattice must consist of layers of FeO_4 tetrahedra united in one direction and attached by oxygen bridges to layers of AlO_6 octahedra at a distance of $1/_4b$. Ca ions are arranged between the layers of octahedra and of tetrahedra, and they cannot be completely saturated coordinately with oxygen atoms.

Malquori and Cirilli [17] studied the structure of $2CaO \cdot Fe_2O_3$, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ by rotation and Weissenberg X-ray diffraction. Table 4 gives the parameters of the lattices (in Angstrom units).

The elementary cell of dicalcium ferrite contains four molecules of $2CaO \cdot Fe_2O_3$ ($Ca_8Fe_4^{IV}Fe_4^{VI}O_{20}$). Nonequivalence of iron atoms along the b axis is found: in the elementary cell of $2CaO \cdot Fe_2O_3$ iron atoms are found in tetrahedral and octahedral coordination with formation of groupings FeO_6, FeO_4, FeO_6, FeO_4 arranged along the b axis and united together through oxygen atoms. In the a direction these groups must be united to analogous groups. The Ca ions are arranged in the same plane (parallel to ac) as the oxygen atoms through which FeO_6 and FeO_4 groups are united.

TABLE 1

Sample No.	Composition of sample		Refractive indices calculated on the assumption that $5CaO \cdot 3Al_2O_3$ enters into solid solution in the form of					
	$5CaO \cdot 3Al_2O_3$, wt. %	$5CaO \cdot 3Al_2O_3$, mole %	the cubic modification			the rhombic modification		
			N_g	N_p	$N_g - N_p$	N_g	N_p	$N_g - N_p$
1	10	8.5	2.04	1.949	0.091	2.047	1.955	0.092
2	20	17.2	2.00	1.917	0.083	2.013	1.93	0.083
3	30	26.2	1.957	1.884	0.073	1.978	1.903	0.075
4	40	35.6	1.913	1.848	0.065	1.942	1.875	0.067
5	50	45.0	1.869	1.813	0.056	1.904	1.846	0.058

TABLE 2

Sample No. *	CaO, wt. %	Al_2O_3, wt. %	Fe_2O_3, wt. %	Al_2O_3/Fe_2O_3 (alumina modulus)
12	50.0	38.0	12.0	3.17
14	49.73	36.27	14.0	2.59
16	49.4	34.6	16.0	2.162
20	48.6	31.4	20.0	1.57
24	47.8	28.2	24.0	1.175
32	46.32	21.68	32.0	0.68
42	44.43	13.57	42.0	0.32

* The Sample No. corresponds to the ferric oxide content of the sample.

Graphs for the dependence of the refractive indices of aluminoferrites on the amount of C_5A_3 going into solid solution with C_4AF.

The elementary cells of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ belong to the type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$, in which $Me^{IV}Me^{VI}$ denotes oron or aluminum atoms having coordination numbers of 4 and 6. The relative numbers of atoms in the elementary cell of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ can be expressed as $Ca_8Fe_4^{IV}Al_4^{VI}O_{20}$, in which iron is in the tetrahedral form and aluminum in the octahedral state of coordination. The relative numbers of atoms in the elementary cell of $2CaO \cdot Fe_2O_3$ can be expressed as $Ca_8Fe_4^{IV}Fe_4^{VI}O_{20}$, in which Fe^{IV} and Fe^{VI} are iron atoms having coordination numbers of 4 and 6, respectively. For the composition $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ (22.8 % of ferric oxide), given by Swayze, and also for the composition $6CaO \cdot 2.1Al_2O_3 \cdot 0.9Fe_2O_3$ (20.7% of ferric oxide), given by Malquori, it did not appear to be possible to assign positions of atoms in an elementary cell of the type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$. It must therefore be considered that Swayze's formula merely gives the proportions of the three oxides.

As regards the structure of the solid solution having the maximum content of aluminate, as determined in this investigation, we must make the following remarks. It is probable that the relative numbers of atoms in the elementary cell of the solid solution of limiting composition can be expressed in the form $Ca_8Fe_2Al_6O_{20}$, corresponding to the type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$, which is common to $2CaO \cdot Fe_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. In fact, the limiting composition of the solid solution, which we have given in the form $6CaO \cdot 2.49Al_2O_3 \cdot 0.77Fe_2O_3$, can be expressed as $7.8CaO \cdot 3.24Al_2O_3 \cdot Fe_2O_3$, a coefficient of unity being taken for ferric oxide. This formula can be expressed approximately as $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3 \cdot (Ca_8Fe_2Al_6O_{20})$. In all probability for such a composition a
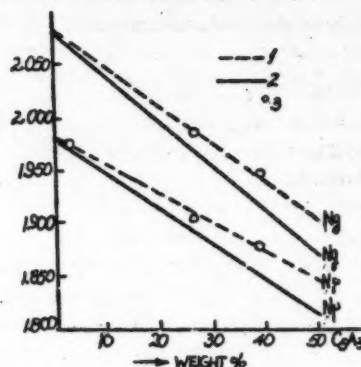
TABLE 3

Sample No.	Refractive indices of aluminoferrites			Composition of aluminoferrites				Formulas of aluminoferrites***	Fe_2O_3 content of aluminoferrite, % by wt.	Ratio $\frac{CaO}{Al_2O_3 + Fe_2O_3}$
	N_g	N_p	$N_g - N_p$	C_5A_3, wt. %	C_4AF,** wt. %	C_5A_3, mol. %	C_4AF, mol. %			
12	1.914	1.854	0.06	47.5	52.5	42.8	57.2	$7.8CaO \cdot 3.24Al_2O_3 \cdot 177Fe_2O_3$	17.2	1.84
14	1.914	1.854	0.06	47.5	52.5	42.8	57.2	$7.8CaO \cdot 3.24Al_2O_3 \cdot 1.77Fe_2O_3$	17.2	1.84
16	1.923	1.863	0.06	44.5	55.5	40.25	59.75	$7.33CaO \cdot 2.98Al_2O_3 \cdot 1.82Fe_2O_3$	18.2	1.84
20	1.946	1.876	0.068	39.0	61.0	34.6	65.4	$6.7CaO \cdot 2.59Al_2O_3 \cdot 1.9 Fe_2O_3$	20.0	1.86
24	1.983	1.900	0.083	29.9	70.1	26.15	73.85	$5.77CaO \cdot 2.06Al_2O_3 \cdot 1.04Fe_2O_3$	23.0	1.92
32		1.973		2.86	97.14	2.39	97.61	$4.12CaO \cdot 1.07Al_2O_3 \cdot 1.45Fe_2O_3$	31.8	2.0

* Abbreviation for $5CaO \cdot 3Al_2O_3$

** Abbreviation for $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

*** A coefficient of unity is assumed for ferric oxide.

TABLE 4

Composition of crystals	a_0	b_0	c_0
$2CaO \cdot Fe_2O_3$	5.32	14.63	5.58
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	5.26	14.42	5.51
$6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$	5.22	14.35	5.48

TABLE 5

Composition	Fe_2O_3, wt. %	No. of molecules in elementary cell	Structural formula (type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$)
$2CaO \cdot Fe_2O_3$	58.8	4	$Ca_8Fe_4^{IV}Fe_4^{VI}O_{20}$
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	32.8	2	$Ca_8Fe_4^{IV}Al_4^{VI}O_{20}$
$8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$	17.5	1	$Ca_8Fe_4^{IV}Al_2^{IV}Al_4^{IV}O_{20}$

TABLE 6

Alumina moduli of clinkers	N_g	N_p	$N_g - N_p$
Clinker from Bakin works	1.942	1.888	0.054
Clinker from Shchurov works	1.959	1.900	0.059
Clinker from Kuvasai works	1.929	1.881	0.048

certain amount of calcium oxide will be held in solid solution. This composition can be taken to be the final member of a series of solid solutions of aluminoferrites; it contains 17.5% by weight of ferric oxide. By the method of crystal optics we have found the value of 17.2% by weight of ferric oxide for such a solid solution. Comparison of these results shows that agreement is quite satisfactory. It is probable that one molecule of $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$ is contained in the elementary cell of the limiting solid solution.

Büssem considers that in the solid solution the aluminum atoms occur only in the octahedral coordination, a view which he based on the structure of tetracalcium aluminoferrite ($Ca_8Fe_4^{IV}Al_4^{VI}O_{20}$). We think that the views of Malquori and Cirilli are more correct, namely, that in aluminoferrites aluminum atoms can have coordination numbers of 6 and 4. In fact, the existence of an aluminoferrite solid solution of the type $Ca_8Fe_2Al_6O_{20}$ confirms this view. Aluminum atoms occur here in tetrahedral (4 atoms) and in octahedral (2 atoms) coordinations. On the basis of the general type $Ca_8Me_4^{IV}Me_4^{VI}O_{20}$, the limiting composition of the solid solution can be represented as $Ca_8Fe_2^{IV}Al_2^{IV}Al_4^{VI}O_{20}$. Table 5 gives members of the series of solid solutions of aluminoferrites together with suggested structural formulas.

The general formula for all three compositions has the form $8CaO \cdot xAl_2O_3 \cdot yFe_2O_3$, in which x varies from 0 to 3 and y from 4 to 1, and the sum $x + y = 4$.

Solid Solutions in the System $3CaO \cdot Al_2O_3 - 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The question of the formation of solid solutions between $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ has not been resolved.

Thus, there are indications in the literature of the formation of solid solutions between tricalcium aluminate and tetracalcium aluminoferrite. McMurdie [5] considers that $3CaO \cdot Al_2O_3$ is soluble to the extent of 2.5-5 % by

weight. A discussion of the solubility of $3CaO \cdot Al_2O_3$ in $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ has been given by Torcpov and Merkov [18]. The elucidation of this matter is of great importance for the structure of clinker. The study of this system is complicated by the incongruent melting of $3CaO \cdot Al_2O_3$.

In the system $3CaO \cdot Al_2O_3 - 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ we have studied three compositions having different alumina moduli (Al_2O_3/ Fe_2O_3 ratios):

1) 50% $3CaO \cdot Al_2O_3$ and 50% $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $Al_2O_3/ Fe_2O_3 = 1.786$

2) 60% $3CaO \cdot Al_2O_3$ and 40% $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $Al_2O_3/ Fc_2O_3 = 2.351$

3) 70% $3CaO \cdot Al_2O_3$ and 30% $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $Al_2O_3/ Fe_2O_3 = 3.314$

In the optical study of these samples in transmitted and reflected light the interesting fact emerged that all three samples contained not only $3CaO \cdot Al_2O_3$, $5CaO \cdot 3Al_2O_3$, and aluminoferrite, but also free calcium oxide. The presence of free calcium oxide can be explained on the assumption that it is not $3CaO \cdot Al_2O_3$ that enters into solid solution with $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, but $5CaO \cdot 3Al_2O_3$, since tricalcium aluminate decomposes when melted. As regards pentacalcium trialuminate, it not only melts without decomposition, but, as Kazumi Mori and Vukio Matsushita supposed [19], it forms associations corresponding to the composition $5CaO \cdot 3Al_2O_3$ in the molten condition.

Finally, we consider that the experiments of Skue [20], carried out at the Institute of Silicate Chemistry on the effect of fluorine compounds on solid solutions of calcium aluminoferrites, provide direct confirmation of the view that $5CaO \cdot 3Al_2O_3$ enters into the composition of the solid solutions of aluminoferrites. Skue showed that, when mixtures of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $6CaO \cdot 2Al_2O_3$ are heated with calcium fluoride, it is always $5CaO \cdot 3Al_2O_3$ that separates, not $3CaO \cdot Al_2O_3$, together with aluminoferrite having an alumina modulus less than those of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$.

In the mixtures that we investigated the refractive indices of the aluminoferrites attained the values. $N_g = 1.973$ and $N_p = 1.916$. The investigation was made in sodium light in phosphorus immersion liquids.

Aluminoferrites of Industrial Cement Clinkers.   As synthetic aluminoferrites are of variable composition, there is reason to suppose that the actual crystals of the aluminoferrite phase of industrial clinkers will be merely one or another of the above-described series of solid solutions. With the object of determining the composition of the aluminoferrite phase, the so-called "heavy"fractions were separated from three samples of industrial clinker. The separation was effected by centrifugation in methylene iodide. Investigation of the "heavy" fractions with the aid of the microscope and of X-rays showed that aluminoferrites of variable composition were present (Table 6).

This fact has great practical importance. Until now, mineralogical composition of clinker has been calculated on the assumption that only $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ is formed in it. We consider that in the quantitative determination of the minerals of clinker, and of its ferrite component in particular, it is necessary to take microscopic investigation as the main basis of the work. Calculation of the mineralogical composition must take account of the formation of an aluminoferrite whose composition will vary from $8CaO \cdot 2Al_2O_3 \cdot 2Fe_2O_3$ (4: 1: 1) and $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$ and can be determined from refractive index measurements. When this method is used for the determination of aluminoferrites in clinker, the accuracy with which the other clinker minerals can be determined is increased. This is very important in the diagnosis of the properties of cement, such as strength, sulfate-stability, etc. A study of the aluminoferrites crystallizing from mixtures containing calcium aluminates and silicates and from mixtures containing an excess of free calcium oxide confirmed that they are of variable composition.

SUMMARY

1. Solid solutions of calcium aluminoferrites are formed with the participation not of the cubic form of $5CaO \cdot 3Al_2O_3$, but of rhombic (a') form (which is structurally closer to $2CaO \cdot Fe_2O_3$ and to $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) the other components being dicalcium ferrite and a certain amount of free calcium oxide.

2. The composition of the aluminoferrite containing the maximum amount of aluminate in solid solution corresponds to 17.5% by weight of ferric oxide. The formula of such an aluminoferrite can be written $8CaO \cdot 3Al_2O_3 \cdot Fe_2O_3$.

3. $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ does not form solid solutions containing $3CaO \cdot Al_2O_3$.

4. Aluminoferrites present in mixtures containing calcium aluminates, calcium silicates, or excess free calcium oxide are of variable composition.

5. The aluminoferrites of industrial clinkers are of variable composition.

6. Calculation of the mineralogical composition of clinker must take into account the formation of an aluminoferrite of the composition indicated by the results of microscopic investigation. This procedure increases the accuracy with which the contents of other clinker minerals can be calculated.

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KINETICS OF BROMINE EXCHANGE IN COMPLEX PLATINUM BROMIDES

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The compounds used in the first study of isotopic exchange in complex compounds in 1939 [1] were complex platinum bromides, in particular, $K_2[PtBr_4]$ and $K_2[PtBr_6]$. It was shown that exchange occurs at a measurable rate in these compounds and that all of the bromine atoms take part in the exchange. In the intervening fifteen years exchange phenomena in complex compounds has been the subject of several investigations both in the USSR and in other countries.

Until recently, however, these investigations have not been closely concerned with the kinetics of the exchange processes. The gathering of kinetic data, i.e. data for the dependence of the exchange rate on the concentration of reactants and on other factors, was begun by Adamson [2], who worked with the complex cyanide $K_3[Mn(CN)_6]$. The first tentative data on the activation energies of exchange reactions of complex platinum compounds were obtained by the present authors in collaboration with Nikolskaya and Kozlova [3].

In the present investigation we have studied the kinetics of exchange in $K_2[PtBr_4]$ and $K_2[PtBr_6]$, the variables examined being time, concentration of complex ion, concentration of free ligand (Br), and temperature. Further experiments were carried out to determine the effect of sunlight on the exchange rate.

EXPERIMENTAL

The procedure was as follows. Active bromine was obtained from irradiated bromobenzene, which was shaken with aqueous KBr, the aqueous layer being then extracted with benzene in order to free it from the organic component. A weighed amount of the pure preparation of complex salt ($K_2[PtBr_4]$ or $K_2[PtBr_6]$) was dissolved in a definite volume of water, and to this solution a solution of KBr of definite concentration and containing Br^{82} tracer was added. The solution was stirred for a definite time at a given temperature in a thermostat protected from the action of light and the complex ion was then separated almost completely from solution by the addition of a suitable precipitant. The $[PtBr_4]^{--}$ ion was precipitated as $[Pt(NH_3)_4][PtBr_4]$ or $[Ni(En)_3][PtBr_4]$. The $[PtBr_6]^{--}$ ion was precipitated as $Cs[PtBr_6]$. The compositions of the precipitated salts and the completeness with which they were separated were established by control experiments, and it was shown by further control experiments that it was unnecessary to make a correction for "zero" (induced) exchange.

After being washed, the precipitated salts were brought into solution, and their activities were measured with a suitable counting arrangement. $[Pt(NH_3)_4][PtBr_4]$ was brought into solution by means of hot caustic alkali, $[Ni(En)_3][PtBr_4]$ also by means of alkali, and $Cs2[PtBr_6]$ by treatment with dilute $Na_2S_2O_3$ solution. Measurements were made not only on the solution of the complex, but also on the mother liquor and on a standard solution ($KBr + KBr^{82}$). The activity balance sheet (adjusted to a given time) was extremely satisfactory. For example, in one experiment the activity of the solution of the complex together with that of the mother solution was 752, whereas the activity of the standard was 766 (all activities are given in impulses per minute). Our results are detailed below.

1. <u>Dependence of Degree of Exchange on Time.</u> As usual, we employ the term "degree of exchange" to mean $I = \dfrac{x_t}{x_\infty}$ in which x_t is the activity of the complex at time t (from the start of the experiment), and x_∞ is attained In Fig. 1, time (minutes) is plotted along the axis of abscissae and $\dfrac{x_t}{x_\infty}$. 100% along the axis of ordinates for $K_2[PtBr_4]$ and for $K_2[PtBr_6]$. In these experiments the concentration of the complex ion was $0.55 \cdot 10^{2}$ mole/liter in each case, and the KBr concentration was $2.2 \cdot 10^{-2}$ mole/liter in the case of $K_2[PtBr_4]$ and $3.3 \cdot 10^{-2}$ mole/liter in the case of $K_2[PtBr_6]$.

In Figures 2 and 3, time (minutes) is again plotted as abscissa, and the ordinate is the negative natural logarithm of $(1-F)$; Fig. 2 refers to $K_2[PtBr_4]$, and Fig. 3 to $K_2[PtBr_6]$. The points in Fig. 1 correspond to separate experiments but those in Figures 2 and 3 represent the averaged results of a whole series of separate experiments.

2. <u>Dependence of the Degree of Exchange on the Concentrations of Reactants.</u> Fig. 4 shows the dependence of the degree of exchange $\dfrac{x_t}{x_\infty}$ 100% on the concentration of $K_2[PtBr_4]$. In all of the experiments of this series the

KBr concentration was kept constant at $2.2 \cdot 10^{-2}$ mole/liter. The experiments were carried out at 20°, and the duration of the exchange reaction was about ten minutes. Fig. 5 shows the dependence of the degree of exchange on KBr concentration. In all of the experiments of this series the concentration of $K_2[PtBr_4]$ was $0.55 \cdot 10^{-2}$ m/l, the temperature was 20°, and the duration of the exchange reaction was 30 minutes. Figures 6 and 7 show the analogous relationships for $K_2[PtBr_6]$. In the experiments illustrated by Fig. 6, the KBr concentration was $3.3 \cdot 10^{-2}$ mole/liter, the temperature was 20°, and the duration of the exchange reaction was about 30 minutes. In the experiments illustrated by Fig. 7 the concentration of $K_2[PtBr_6]$ was $0.77 \cdot 10^{-2}$ mole/liter.

3. Dependence of the Degree of Exchange on Temperature. In Fig. 8 temperature is plotted as abscissa and degree of exchange as ordinate for $K_2[PtBr_4]$ and $K_2[PtBr_6]$. Figure 9 differs from Fig. 8 in that the natural logarithm of the degree of exchange is plotted as ordinate.

4. Dependence of the Degree of Exchange on the "Age" of the Solution. After most of the results given above had been obtained, a new effect was discovered, it being found that the degree of exchange depends on the "age" of the solution of the complex, i.e. on the time elapsing from the preparation of the solution to the start of the exchange experiment. This effect was detected in $K_2[PtBr_4]$ solutions. In solutions that were let stand, the degree of exchange was greater than in freshly prepared solutions, other conditions remaining constant. Our results are given in the table. Preliminary experiments showed that a similar effect occurs to some extent in the case of $K_2[PtBr_6]$. After we had discovered this effect we learnt that a similar phenomenon had been observed independently by Adamson and Wilkins [4] for thiocyanato-pentammines of cobalt and chromium.

5. Effect of Light. As already stated, the exchange experiments described above were carried out in a thermostat protected from the action of light. It was shown by special experiments that for $K_2[PtBr_4]$ the same results are obtained whether the exchange reaction occurs in the light or in the dark.

Light has an appreciable effect on bromine exchange in K_2PtBr_6. Thus, at a K_2PtBr_6 concentration of $0.55 \cdot 10^{-2}$ mole/liter and a KBr concentration of $3.3 \cdot 10^{-2}$ mole/liter (at 20° for 30 minutes) the extent of exchange is on the average 30% in the dark, but is appreciably higher, varying from 45% to 75% in individual cases, in the light. The variation observed may be due to variation in the intensity of illumination in different experiments. The effect of light on bromine exchange in K_2PtBr_6 is under further investigation.

DISCUSSION OF RESULTS

It must be pointed out that the values that we have obtained for the exchange rate in dilute solutions of $K_2[PtBr_4]$ are appreciably lower than those obtained in the first investigation by Grinberg and Filinov [1]. This discrepancy may be attributed in part to the increased accuracy of measurement now possible, as compared to that possible in 1939. However, this is probably not the only factor concerned. Rich and Taube [5] recently pointed out the important part played by impurities, which may have a catalytic effect on the exchange. We are studying this matter further at the present time. In the present work, however, $K_2[PtBr_4]$ was prepared on many occasions and all of the samples behaved identically.

Comparison of the data given in this paper with that of Grinberg and Nikolskaya [6] brings out clearly the high degree of dependence of the exchange rate of $K_2[PtBr_4]$ on the total concentration of atoms undergoing exchange. In fact, according to the results of Grinberg and Nikolskaya [6], the time for the practical attainment of equilibrium is about 40 minutes for $C_{K_2PtBr_4} = 0.5 \cdot 10^{-1}$ mole/liter and $C_{KBr} = 2 \cdot 10^{-1}$ mole/liter, the half-exchange period calculated from these results being about 7-9 minutes; on the other hand, according to Fig. 1 the half-exchange period for $K_2[PtBr_4]$ ($C = 0.55 \cdot 10^{-2}$ mole/liter) is 120 minutes (Fig. 10).

When we take into account the qualitative character of the results obtained previously and the absence of thermostatic control in the experiments of Grinberg and Nikolskaya, we can undoubtedly conclude that the half-exchange period of $K_2[PtBr_4]$ is highly dependent on the total concentration of the atoms undergoing exchange. The form of this dependence appears to be close to that required for a bimolecular reaction. It will be seen from Figures 1 and 2 that, under the conditions studied, the exchange process in $K_2[PtBr_4]$ is satisfactorily described by the fundamental equation for simple exchange, i.e.

$$-\ln(1-F) = Rt \frac{a+b}{ab}$$

For the given temperature conditions and concentrations (see Figures 1 and 2) R is close to $0.5 \cdot 10^{-4}$ g-atom of bromine per liter per minute. By dividing this value by the molar concentration of the complex, we arrive at the value of $K = \dfrac{R}{C}$. As regards the variation in the extent of exchange with $K_2[PtBr_4]$ with time, however, there is some departure from the usual exponential relationship. The way in which the extent of exchange increases with

time indicates the possibility of the participation of a chain mechanism in the process. In this case it is not possible, in general, to calculate the value of R on the basis of the law of simple exchange. However, an approximate tentative value of R can be obtained on the assumption that in this case $\ln(1-F)$ is a linear function of time. This tentative calculation gives values of R of the order of $2\text{-}3 \cdot 10^{-4}$ g-atom of bromine per liter per minute. In any case it is clear that the exchange rate in $K_2[PtBr_6]$ is considerably higher than in $K_2[PtBr_4]$. The graphs given above show that at a concentration of the complex of $0.55 \cdot 10^{-2}$ mole/liter and at $20°$, the half-exchange period for $K_2[PtBr_4]$ is about 120 minutes, whereas for $K_2[PtBr_6]$ it is about 50 minutes (see Fig. 10). With respect to the extent of breakdown into ions, $[PtBr_6]^{--}$ must be more stable than $[PtBr_4]^{--}$. Hence, we again meet with the fact, established previously, that the degree of instability (instability constant) of a complex is not bound in any way to determine the rate with which it undergoes exchange. We shall return to this question later.

The graphs indicate that the degree of exchange, both of $K_2[PtBr_4]$, and of $K_2[PtBr_6]$, is approximately proportional to the concentration of the complex under the conditions studied. A simple relationship of this kind is to be expected when the comparatively low degrees of exchange are taken into account. It cannot be doubted that the linear relationship between the degree of exchange and the concentration of the complex represents a first approximation. This view is confirmed by experiments that we have carried out recently: at higher concentrations of $K_2[PtBr_4]$ the exchange rate is probably proportional not to the first power of this concentration, but to a higher power.

As regards the dependence of the degree of exchange on the concentration of free ligand (Br^-) , it is almost absent in the case of $K_2[PtBr_4]$, but is very marked in the case of $K_2[PtBr_6]$. This fact again emphasizes the undoubted difference in the mechanism of exchange in such closely related complex compounds as $K_2[PtBr_4]$ and $K_2[PtBr_6]$. When the above-mentioned newly discovered effect is taken into account, the almost complete independence of the degree of exchange in $K_2[PtBr_4]$ on the KBr concentration may be explained on the assumption that the exchange rate is determined by the rate of a slower aquation process. The rate at which bromide ions enter and leave the inner sphere is apparently much greater than the rate of the primary interaction of the $[PtBr_4]^{--}$ ion with water. Our results indicate that, in the dilute solutions studied, the mechanism of reaction via intermediate formation of $K_3[PtBr_5]$ plays a very small part in comparison with that of reaction via aquo ions.

As regards $K_2[PtBr_6]$, it is probable that exchange by an oxidation-reduction mechanism plays an important part. Many years ago Grinberg, Ptitsyn, and Lavrentyev [7] showed that hexahaloplatinates $K_2[PtX_6]$ dissociate in solution with liberation of free halogen in accordance with the equation $K_2[PtX_6] \rightleftarrows K_2[PtX_4] + X_2$. For differing X (Cl,Br,SCN,I) the degree of dissociation differed, increasing from chlorine to iodine. For $K_2[PtBr_6]$ the equilibrium bromine concentration determined from the oxidation-reduction potential is about 10^{-14}; for $K_2[PtI_6]$ the equilibrium iodine concentration is 10^{-5}.

It is characteristic of hexahaloplatinates that their stabilities with respect to breakdown into ions increase from chlorine to iodine, whereas their thermal stabilities decrease in this direction. The dependence of the degree of exchange on the KBr concentration, the tentative values of activation energy given below, and also the experimentally established high degree of dependence of the extent of exchange on the intensity of illumination are all in accord with the view that an oxidation-reduction mechanism plays an important part in the exchange of $K_2[PtBr_6]$ with bromide ions.

Earlier investigations by Grinberg and Filinov [8] showed that the interaction of compounds of a given metal in different stages of oxidation often passes through a stage of intermediate compounds of the quinhydrone type. Thus, by careful oxidation of $[Pt(NH_3)_2Br_2]$ under suitable conditions, or by careful reduction of $[Pt(NH_3)_2Br_4]$, it is easy to isolate "molecular" compounds of the type $[Pt(NH_3)_2Br_2]$. $[Pt(NH_3)_2Br_4]$. The existence of such compounds has been established in the majority of cases. It is quite possible that products of a similar type are formed also during the reduction of $K_2[PtBr_6]$. In fact, it is difficult to imagine the elimination of a Br_2 molecule from $K_2[PtBr_6]$ as an elementary act. It is obvious that a single atom of bromine must first split off with the intermediate formation (very transitory, possibly) of a tervalent platinum derivative in accordance with the scheme: $[PtBr_6]^{--} \rightleftarrows [PtBr_5]^{--} + Br^-$. The $[PtBr_5]^{--}$ ions must be unstable. They may decompose according to the scheme: $2PtBr_5 \rightleftarrows [PtBr_6] \rightleftarrows [PtBr_4]^{--}$. The atomic bromine eliminated may react with the solvent according to the schemes: $Br^- + H_2O \rightleftarrows HBr + OH$ and $Br^* + H_2O \rightleftarrows OHBr + H$, and it may react also with bromide ions. The probability of the last reaction increases as the KBr concentration is increased. We may here postulate the formation of the simplest polyhalide ion Br_2^-.

The intermediate formation of ions of the type $[PtCl_5]^{--}$ was postulated by Rich and Taube [5] in a recently published paper, in which they make no mention of our investigations on the interaction of compounds of a given metal in different states of oxidation, nor of our work on chlorine exchange in the $[PtCl_4]^{--}$ ion.
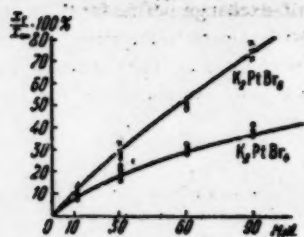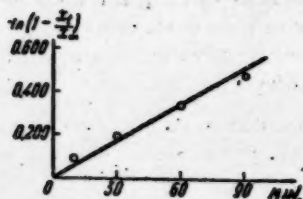
Fig. 1.

Fig. 2.
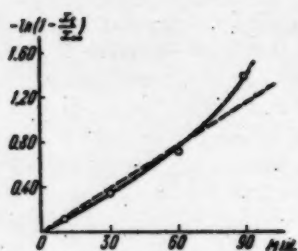
Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

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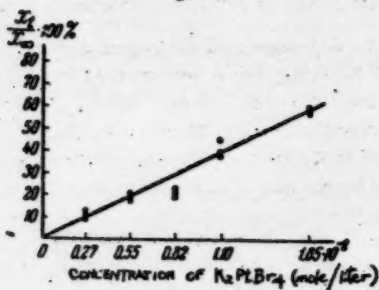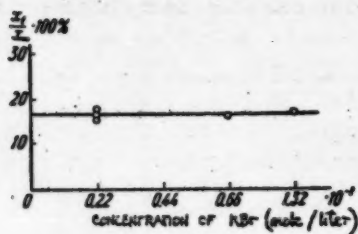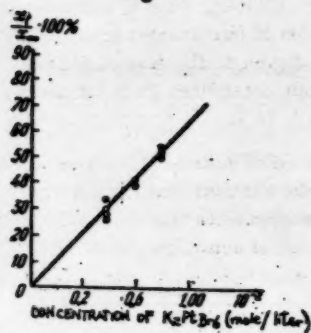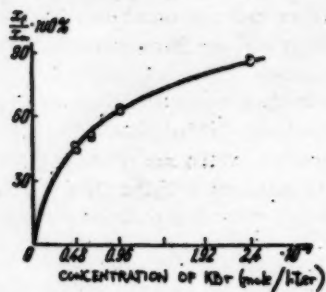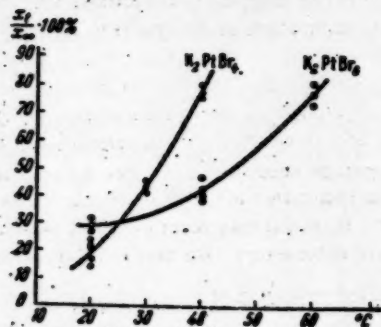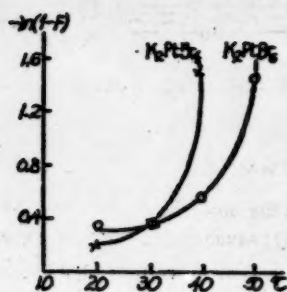
Fig. 9
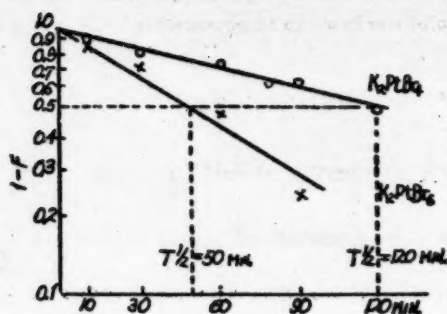
Fig. 10

TABLE

Time from moment of dissolution to start of exchange	Activity of complex (without background) (impulses/minute)	Activity of standard (without background) (impulses/minute)	$\frac{x_t}{x_\infty} \cdot 100\%$	$i = \frac{x_t}{x_\infty}$
10–15 minutes	152	1410	21	
	204	2700	16 av. 18±7	0.82
	500	5720	17	
24 hours	635	3824	33	
	468	2640	35 av. 35±6	0.65
	500	2600	38	
48 hours	340	1730	40	
	360	1732	42 av. 41±7	0.59

We do not assert that exchange in $K_2[PtBr_4]$ occurs <u>exclusively</u> by an oxidation-reduction mechanism, but we emphasize the importance of the part played by this process in the general (possibly more complex) process.

Tentative calculations of activation energies were made with the aid of the Arrhenius equation:

$$E = \frac{2,3\, RT_1 T_2}{T_2 - T_1} \quad \log \frac{K_2}{K_1} \cdot \ast$$

According to our results, the activation energy for $K_2[PtBr_4]$ is about 17 kcal/mole, and that for $K_2[PtBr_6]$ varies from 4 to 10 kcal/mole.

SUMMARY

1. Experimental data have been obtained with the object of elucidating the dependence of the extent of isotopic exchange of bromine in $K_2[PtBr_4]$ and $K_2[PtBr_6]$ (aqueous solutions) on the duration of the exchange reaction, the concentration of the complex ion, the concentration of bromide ions, the temperature, and the presence of sunlight. An exchange-acceleration effect was detected in aqueous solutions of $K_2[PtBr_4]$ that had been allowed to stand.

2. On the basis of the data obtained, tentative calculations were made of the activation energies of the exchange process in the $[PtBr_4]^{--}$ and $[PtBr_6]^{--}$ ions. Under the conditions studied the activation energy for bromine exchange in the $[PtBr_6]^{--}$ ion (4-10 kcal/mole) was found to be appreciably less than the activation energy for the $[PtBr_4]^{--}$ ion (about 17 kcal/mole).

3. On the basis of the data obtained it is concluded that the mechanism of the exchange reaction is different in the $[PtBr_4]^{--}$ and $[PtBr_6]^{--}$ ions.

4. Over the concentration range studied, exchange with $K_2[PtBr_4]$ in aqueous solution proceeds to a large extent though the intermediate formation of aquo ions.

5. The character of the dependence of the degree of exchange on the bromide ion concentration, the values obtained for the activation energy, the effect of sunlight on the degree of exchange, and also some previously studied properties of quadrivalent platinum derivatives enable us to postulate that exchange with $K_2[PtBr_6]$ proceeds mainly via an oxidation-reduction equilibrium.

6. The data obtained in this work for the $[PtBr_4]^{--}$ and $[PtBr_6]^{--}$ ions again confirm the conclusion first reached by Grinberg and Nikolskaya, namely, that the instability of a complex ion, as measured by its instability constant, by no means always determines the rate at which it undergoes exchange.

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$\ast$ In place of K_2 and K_1 we put values of R from the equation. $-\ln(1-F) = Rt\, \dfrac{a+b}{ab}$.

REACTIONS OF FENCHONE WITH ORGANOMAGNESIUM AND ORGANOLITHIUM COMPOUNDS

COMPOUNDS

A. N. Nesmeyanov, V. A. Sazonova, and R. B. Materikova

We have shown previously [1] that in the reaction of a Grignard reagent with a carbonyl compound it is not possible to isolate a complex compound of the type.

$$\begin{array}{c} R' \\ \diagdown \\ C = O \cdot R''' MgX \cdot Ether \\ \diagup \\ R'' \end{array}$$
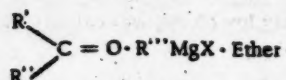
and that the intermediate compounds described by Hess [2], Meisenheimer [3], and others as complexes are of the alkoxide type.

$$\begin{array}{c} R' \\ \diagdown \\ R'' - C - OMgX \cdot Ether \\ \diagup \\ R''' \end{array}$$
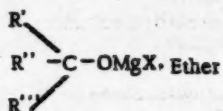
as supposed by Grignard.

Klages [4] was in error in affirming the existence of the complex.
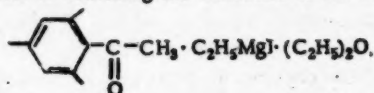
Fuson and coworkers [5] showed that in this case the substance formed was the enolate of 2′, 4′, 6′-trimethylaceto-phenone
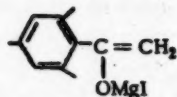
and not a complex formed with an organomagnesium compound. There remains the complex of a carbonyl compound with a Grignard reagent described by Leroide [6], namely, the addition product formed by fenchone with phenylmagnesium bromide

As this case was in conflict with our results and there were independent reasons for doubting it, we set ourselves the task of determining the structure of this compound, the study of which we had undertaken previously but had not completed.

Leroide writes: "Fenchone reacts with aromatic organomagnesium compounds to give addition products that are insoluble in ether and hydrocarbons. When these derivatives are treated with water, fenchone is regenerated and the hydrocarbon corresponding to the organomagnesium compound used is formed. The following compounds were prepared:

$C_6H_5MgBR \cdot C_{10}H_{16}O$;   o-$CH_3C_6H_4MgBr \cdot C_{10}H_{16}O$;   p-$CH_3C_6H_4MgBr \cdot C_{10}H_{16}C$.
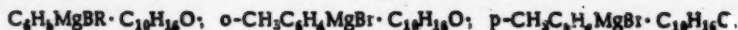
By prolonged heating in presence of a large amount of solvent these compounds were converted into magnesium derivatives of tertiary alcohols.".

As the author does not give any analysis, does not discuss the separation of these precipitates, and apparently worked with the reaction mixture, the hydrocarbon that he found in the decomposition products can be accounted for by unchanged organomagnesium compound present in the solution, especially when we take into account the

fact that very little precipitate was obtained; there can be no doubt that fenchone also would then be obtained. When the reaction mixture was heated for a long time (60 hours in a mixture of ether and toluene for the phenyl derivative), Leroide succeeded in obtaining small amounts of tertiary alcohols (7% for 2-phenylfenchyl alcohol). There is no proof, however, that these alcohols were formed from the precipitate and not from the fenchone and phenylmagnesium bromide present in the solution.

In our work we tried to avoid the errors made by Leroide. All experiments requiring the absence of oxygen and moisture were carried out in an atmosphere of pure dry nitrogen. The precipitate was filtered off through a sintered glass filter, washed repeatedly with absolute ether, dried in a current of nitrogen, and analyzed. The further work was carried out solely with this precipitate.

Experiment showed that the analysis of the precipitate was far-moved from that required by Leroide's formula and also from that required by the magnesium derivative of the tertiary alcohol: The Mg: Br ratio found was 1:1.4 (Br 40.68%, Mg 8.80%); but for the complex postulated by Leroide we ought to have obtained Br 24.02%, Mg 7.27% (Mg: Br ratio, 1:1). The yield of precipitate was very low (3.6%, was calculated as $C_6H_5MgBr \cdot C_{10}H_{16}O$). When the solution filtered from the precipitate was rapidly poured into another vessel in the open air, a further small amount of the same precipitate separated after a short time. The small amount in which this substance was formed, the slow formation of further precipitate when the filtrate was allowed to stand in the air, and the pressure of appreciable amounts of biphenyl in the solution — all these facts suggested that the formation of the precipitate was associated with oxidative processes. In fact, when the reaction was carried out under the usual conditions, without the use of nitrogen, considerably more precipitate was obtained and, moreover, its separation was gradual.

When the substance was decomposed with water, ether and fenchone were obtained, and no benzene was detected. It was found that fenchone could be displaced from the complex by means of benzophenone, but no triphenylmethanol was then formed, though this would be the product of the reaction of benzophenone with the phenylmagnesium bromide considered by Leroide to be present in the complex. Benzil also displaced fenchone from the complex, but again no 2-hydroxy-2,2-diphenylacetophenone was detected (benzilic acid was unexpectedly obtained). It was found that, under similar conditions, benzil rearrangement occurred also when benzil was treated with the basic magnesium salt $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$. The occurrence of the benzil rearrangement under the action of such weakly alkaline reagents has not been reported in the literature.

The evident absence of phenylmagnesium bromide in the precipitate, the complex nature of the precipitate as indicated by the ease with which fenchone is separated from it by the action of substituting reagents (water, ketones), and the association of the formation of the precipitate with oxidative processes — all these facts point to the conclusion that the precipitate is a complex of fenchone with a basic magnesium salt [$MgBr_2 \cdot MgBrOH \cdot 2C_{10}H_{16}O(C_2H_5)_2O$] and not with phenylmagnesium bromide as maintained by Leroide. It was found, in fact, that treatment of fenchone with a salt of composition $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$, prepared by careful oxidation of an ethereal solution of phenylmagnesium bromide with atmospheric oxygen, results in the formation of a complex containing fenchone which is identical in properties with the precipitate studied.

As stated at the beginning, in the reactions of fenchone with phenylmagnesium bromide, o-tolymagnesium bromide, and p-tolymagnesium bromide, the corresponding tertiary alcohols are obtained only in very low yield. In 1946 in connection with investigations on the properties of terpenes, Nametkin and Obtemperanskaya [7] improved the procedure for the Grignard reaction by replacing diethyl ether by dibutyl ether, so that the reaction temperature could be raised to 110°; also, they used a twofold excess of phenylmagnesium bromide in the reaction. In this way they succeeded in raising the yield of tertiary alcohol from 7% to 36%.

For the synthesis of 2-phenyl- and 2-p-tolyl-fenchyl alcohols we used organolithium compounds:

Very mild reaction conditions were used: fenchone was added gradually at room temperature to an ethereal solution of phenyl- or p-tolyl-lithium, the mixture was stirred for 30 minutes, and the reaction mixture was decomposed with water. The arylfenchyl alcohols were obtained in good yield (70%).

EXPERIMENTAL

Reaction of Fenchone with Phenylmagnesium Bromide. Fenchone (15.2 g' was added to 53.3 ml of a filtered ethereal solution of phenylmagnesium bromide (0.3395 g of C_6H_5MgBr per ml', A crystalline precipitate(1.2 g)was formed; it was filtered off, washed six times with ether, and dried in a current of nitrogen. When immersed in dry Vaseline under the microscope, the crystals were seen to be regular six-sided plates.

Found %: Br 50.68, Mg 8.80

The precipitate was not soluble in ether, benzene, or dioxane; it was soluble in molten benzophenone and benzil, but reaction occurred with liberation of fenchone. Decomposition of the precipitate with ammonium chloride solution yielded ether and fenchone.

Displacement of Fenchone from the Complex by means of Benzophenone. To 5 g of molten benzophenone. 2 g of the precipitate was obtained by reaction of fenchone with phenylmagnesium bromide was added, Frothing occurred, and the precipitate dissolved. The resulting mixture was vacuum-distilled (in a current of nitrogen). At 81° (21 mm) 0.55 g of fenchone came over, and 4.4 g of unchanged benzophenone, m.p. 45°, was recovered; it did not give a red color with concentrated sulfuric acid, which indicated that no triphenylmethanol was present,even as impurity. This again confirms the absence of Grignard reagent in the precipitate.

Reaction of Benzil with the Complex. To 1.1630 g of benzil (m.p. 93°), which was melted in a Claisen flask, 1.7 g of the complex obtained by reaction of fenchone with phenylmagnesium bromide was added gradually. Frothing of the mixture occurred, and this was followed by dissolution of the precipitate in the benzil. The solution assumed a reddish-brown color. In order to effect complete removal of ether, the mixture was heated carefully. At 81° (21 mm) 0.45 g of fenchone came over. The residue was cooled, and 2 N HCl and ether were added. The ether layer was separated, and the aqueous layer was extracted twice with ether. The ether layers were treated with 10% NaOH solution, and the alkaline extract was acidified with concentrated hydrochloric acid. Benzilic acid (0.55 g; m.p. 149°) was obtained. In a mixture test with authentic benzilic acid it showed no depression of melting point.

Preparation of $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$. An ethereal solution of phenylmagnesium bromide prepared from 6 g of magnesium and 39 g of bromobenzene in 120 ml of absolute ether was filtered and transferred to the reaction flask. Air freed from CO_2 was passed very slowly over the surface of the solution. From time to time the stirrer was switched on in order to renew the surface. After three hours large crystals began to be precipitated. The experiment was continued for two days. The crystals were filtered off, washed several times with small amounts of absolute ether until the odor of biphenyl disappeared, and dried in a current of nitrogen. Weight of precipitate 8.4 g.

Found %: Br 52.72, Mg 10.73.

These results are in close accord with Holroyd's formula [8] $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$ and with his experimental results: Br 53%, Mg 10.86%. The dried precipitate was a crystalline powder, insoluble in the usual organic solvents. It warmed up spontaneously in the air. When it was decomposed with water, ether separated.

Action of Fenchone on $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$. Fenchone (11 4 g) and absolute ether (100 ml) were added to 8.55 g of $MgBr_2 \cdot MgBrOH \cdot 2(C_2H_5)_2O$ contained in a bottle with a-ground-in stopper. The mixture was shaken for 30 hours. The precipitate was filtered off, washed six times with ether, and dried in a current of nitrogen. The product was a colorless powder smelling of fenchone.

Found %: Br 41.21, Mg 9.33

The complex salt became liquid when exposed to air, and it yielded ether and fenchone when decomposed with water. In its properties (decomposition by water, displacement of fenchone by benzophenone and benzil) it was identical with the substance obtained by reaction of phenylmagnesium bromide with fenchone.

2-Phenylfenchyl Alcohol. The experiment was carried out in an atmosphere of nitrogen. An ethereal solution of phenyllithium prepared from 5 g of lithium, 50 g of bromobenzene, and 100 ml of absolute ether was filtered into a Schlenk vessel. The concentration was determined acidimetrically and found to be 0.0933 g of C_6H_5Li per ml. Into the reaction flask 6.87 g (0.08 mole) of phenyllithium was transferred in the form of the above-described ethereal solution. The solution was stirred, and 10 g (0.065 mole) of fenchone was added through a dropping funnel. The reaction mixture was then stirred at room temperature for 30 minutes. Water was added, and the ether layer was separated, washed with water, and dried with magnesium sulfate. Ether was distilled off, and the residue, vacuum-distilled, yielded 10.6 g (70%) of 2-phenylfenchyl alcohol, b.p. 167-168° (14 mm) (the literature [6] gives 166-167° (13 mm).

<u>2-p-Tolylfenchyl Alcohol.</u> p-Tolyllithium was prepared similarly to phenyllithium from 2 g of lithium, 24 g of p-bromotoluene, and 70 ml of absolute ether. The solution was allowed to stand for a short time and then filtered into a Schlenk vessel. The concentration, found acidimetrically, was 0.0653 g of $CH_3C_6H_4Li$ per ml.

Into the reaction flask, 5.91 g (0.06 mole) of p-tolyllithium was transferred in the form of the ethereal solution, and 7.34 g (0.048 mole) of fenchone was added with stirring; there was a slight evolution of heat. Stirring was continued for a further 30 minutes at room temperature. The reaction mixture was decomposed with water, and the ether layer was separated, washed with water, and dried with magnesium sulfate. Ether was distilled off, and the residue, vacuum-distilled, yielded 8.17 g (69%) of 2-p-tolylfenchyl alcohol, b.p. 177° (15 mm) and m.p. 47-52°.

$C_{17}H_{22}O$.

Found %: C 83.61, H 9.30
Calculated %: C 83.61, H 9.84

This tertiary alcohol is readily soluble in the usual organic solvents. The literature [6] gives b.p. 180-181° (15 mm).

SUMMARY

1. The precipitate formed by reaction of phenylmagnesium bromide with fenchone was investigated, and it was shown that, contrary to Leroide's view, this substance is not a complex of fenchone with phenylmagnesium bromide, but is a complex formed between a basic magnesium salt, magnesium bromide and fenchone.

2. 2-Phenyl- and 2-p-tolyl-fenchyl alcohols were prepared in good yield with the aid of organolithium compounds.

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CONDENSATION OF 3,3,3-TRICHLOROPROPENE WITH AROMATIC COMPOUNDS

A. N. Nesmeyanov, R. Kh. Freidlina, and N. A. Semenov

Two authors of this paper have shown, in collaboration with Firstov [1], that 3,3,3-trichloropropene condenses with benzene in presence of a small amount of aluminum chloride with formation of 1,1-dichloro-3-phenylpropene. We considered that this reaction might be of interest as a method of synthesis, permitting the introduction of the reactive grouping $-CH_2CH=CCl_2$, which, in particular, is readily converted into a propionic acid residue — into an aromatic molecule. We have therefore studied the reactions of 3,3,3-trichloropropene with chlorobenzene, bromobenzene, anisole, and phenol.

The reactions of bromobenzene and of chlorobenzene with 3,3,3-trichloropropene in presence of aluminum chloride proceed very vigorously with evolution of heat. The main products isolated were 3-p-bromophenyl-1, 1-dichloropropene and 1,1-dichloro-3-p-chlorophenylpropene, respectively. The structures of these products were proved by hydrolysis with concentrated sulfuric acid, which gave good yields of p-bromo- and p-chloro-hydrocinnamic acids, which were then converted into 6-bromo- and 6-chloro-1-indanones. 1,1-Dichloro-3-p-chlorophenylpropene and 3-p-bromophenyl-1,1-dichloropropene add chlorine with formation of 1,1,1,2-tetrachloro-3--p-chlorophenylpropane and 3-p-bromophenyl-1,1,1,2-tetrachloropropane, respectively. The reactions of anisole and phenol with 3,3,3-trichloropropene in presence of aluminum chloride are slower than those of chloro- and bromo-benzenes, and for complete reaction several hours at 80-90° are required. The compound obtained from anisole was found to be 1,1-dichloro-3-p-methoxyphenylpropene, its structure being proved by its oxidation to p--anisic acid with 5% alkaline potassium permanganate. The condensation of 3,3,3-trichloropropene with phenol proceeded when the mixture was heated, even when aluminum chloride was absent, but it was found to be best to carry out the reaction in its presence. Both o- and p-(3,3-dichloroallyl)phenols were isolated. The structures of these compounds were proved by their alkylation with dimethyl sulfate to 1,1-dichloro-3-o-methoxyphenylpropene and 1,1-dichloro-3-p-methoxyphenylpropene, respectively, which were oxidized to the corresponding o- and p-anisic acids. When 1,1-dichloro-3-p-methoxylphenylpropene was hydrolyzed with concentrated sulfuric acid, the product was a p-methoxyhydrocinnamic acid sulfonated in the nucleus, which was isolated as its barium salt. When 3,3,3-trichloropropene reacted with an aqueous solution of sodium phenoxide, both C— and O-alkylation products were formed, the product being a mixture containing o- and p-(3,3-dichloroallyl)phenols together with 1,1-dichloro-3-phenoxypropene.

The same products were obtained when the same aromatic compounds were caused to react with 1,1,3-trichloropropene, but reaction did not occur so readily and the yields were lower than in the reactions with 3,3,3-trichloropropene. The fact that the reaction of 3,3,3-trichloropropene occurs in absence of aluminum chloride is very interesting. In all cases reaction proceeded with allyl rearrangement and formation of compounds containing the 2,2-dichlorovinyl group. The formation of C-derivatives in the reaction of 3,3,3-trichloropropene with phenol and sodium phenoxide obviously proceeded by the mechanism of reaction-center transfer in both of the reacting molecules:
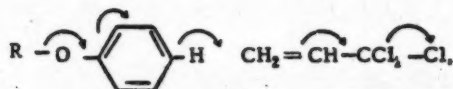
in which R is H or Na.

EXPERIMENTAL

Condensation of Bromobenzene with 3,3,3-Trichloropropene (Preparation of 3-p-Bromophenyl-1,1-dichloropropene). Anhydrous aluminum chloride (1 g) was added to a vigorously stirred mixture of 45 g (0.31 mole) of 3,3,3-trichloropropene and 196 g (1.24 moles) of dry bromobenzene. Vigorous evolution of hydrogen chloride set in, and reaction was complete in 5-10 minutes. The cooled reaction mixture was treated with water, and the lower

layer was separated and dried over calcium chloride. Bromobenzene was distilled off, and the residue was vacuum-distilled. A second distillation yielded 61 g (76%) of a substance having b.p. 117.5-118° (5 mm), n_D^{20} 1.5830; and d_4^{20} 1.5532.

$$C_9H_7BrCl_2\lceil_4^-.$$
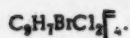
Found: MR 57.23
Calculated: MR 57.19

$$C_9H_7Bl_2Br.$$

Found%: C 40.59; 40.61, H 2.71; 2.73;
Halogen   56, 76; 56, 77
Calculated%: C 40.64; H 2.65; Halogen 56.71
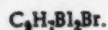
Hydrolysis of 3-p-Bromophenyl-1,1-dichloropropene to p-Bromohydrocinnamic Acid.

A vigorously stirred mixture of the product of the previous experiment (20 g) and 93% sulfuric acid (50 g) was heated at 120° for one hour. The reaction mixture was cooled and poured into water, and the acid that separated was filtered off, washed, and dried. The yield of crude acid was 16.7 g (93%). The acid, recrystallized from heptane, melted at 135°. For p-bromohydrocinnamic acid the literature [2] gives m.p. 136°.

$$C_9H_9O_2Br.$$

Found%: C 47.50; 47.81, H 4.15; 4.09;
H3.96; Br 34.88
Calculated%: C 47.18; Br 34.54; 34.50
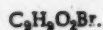
Dehydration of 6 g of the crude acid with concentrated sulfuric acid at 145° yielded 3.5 g (63%) of 6-bromo--1-indanone, melting at 111-112° after crystallization from aqueous alcohol. For 6-bromo-1-indanone the literature [3] gives m.p. 111-112°.

$$C_9H_7OBr.$$

Found%: C 51.25; 51.03; H 3.50; 3.47; Br 37.51;
37.66
Calculated%: C 51.21;   H 3.34;   Br 37.86

Addition of Chlorine to 3-p-Bromophenyl-1,1-dichloropropene (Preparation of 3-p- Bromophenyl-1,1,1,2-tetrachloropropane).

A strong current of chlorine was passed for six hours through 40 g (0.15 mole) of 3-p-bromophenyl--1,1-dichloropropene at 60°, and the resulting increase in weight was 9.6 g (0.13 mole). The reaction mixture was cooled and a crystalline precipitate formed, which was separated and crystallized three times from ethanol. The product, amounting to 32 g (65%), melted at 89°.

$$C_9H_7Cl_4Br.$$

Found%: C 31.58; 31.53; H 2.16 2.13; Halogen 65.95; 65.75
Calculated%: C 32.08;   H 2.10;   Halogen 65.82
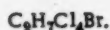
Condensation of Chlorobenzene with 3,3,3-Trichloropropene (Preparation of 1,1-Dichloro-3-p-chlorophenyl-propene.

Reaction between 45 g (0.31 mole) of 3,3,3-trichloropropene and 180 g of chlorobenzene in presence of 1 g of aluminum chloride proceeded with evolution of heat, and in order to carry it out smoothly it was necessary to cool the reaction mixture. Reaction was complete in 5-10 minutes, and the calculated amount of hydrogen chloride was evolved. The reaction product was isolated as in the experiment with bromobenzene, and 51.2 g (74.5%), b.p. 115-116° (6 mm), was obtained in addition to 11 g of residue. The isolated compound had n_D^{20} 1.5630 and d_4^{20} 1.3208.

$$C_9H_7Cl_3\lceil_4^-.$$
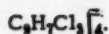
Found MR 54.47
Calculated MR 54.30
Found%; C 48.71; 48.94; H 3.24; 3.34; Cl 47.60; 48 04

$$C_9H_7Cl_3.$$

Calculated%: C 48.79;   H 3.19;   Cl 48.02

Hydrolysis of 1,1-Dichloro-3,p-chlorophenylpropene to p-Chlorohydrocinnamic Acid.

A vigorously stirred mixture of the product of the previous experiment (18 g) and 93% sulfuric acid (60 g) was heated at 110° for 45 minutes. The reaction mixture was cooled and poured onto ice, and the acid that separated was filtered off, washed and dried. The yield of crude product was 12.3 g (82%). Recrystallization from aqueous alcohol and from heptane yielded a substance melting at 122.5-123°. For p-chlorohydrocinnamic acid the literature [4] gives m.p. 122°.

Found %: C 58.55; 58.38; H 5.06; 5.01
$C_9H_9O_2Cl$.   Calculated %: C 58.55;   H 4.91

A sample of the acid was heated with twelve times its weight of concentrated sulfuric acid at 180°, and 6-
-chloro-1-indanone, m.p. 79-80° (from alcohol), was obtained. For 6-chloro-1-indanone the literature [4] gives
m.p. 79-80°.

Addition of Chlorine to 1,1-Dichloro-3-p-chlorophenylpropene (Preparation of 1,1,1,2-Tetrachloro-3 p-chloro-
phenylpropane. Chlorine was passed through 79 g of 1,1-dichloro-3-p-chlorophenylpropene, the temperature of the
mixture being maintained at 30° by cooling. When an increase in weight of 25 g had been attained (two hours), the
reaction mixture was cooled, and the crystalline precipitate was separated. Distillation at 142-143° (5 mm) yielded
81 g (78%) of product, which melted at 90° after repeated recrystallization from ethanol.

Found %: C 37.14; 37.34; H 2.87; 2.85; Cl 61.04; 61.04
$C_9H_7Cl_5$.   Calculated %: 36.96;   H 2.41;   Cl 60.63

Condensation of Anisole with 3,3,3-Trichloropropene (Preparation of 1,1-Dichloro-3-p-methoxyphenylpropene.
A mixture of 44 g (0.30 mole) of 3,3,3-trichloropropene, 93 g (0.86 mole) of anisole, and 2 g of aluminum chloride
was heated at 90° for three hours. In the course of the reaction a further 5 g of aluminum chloride was added. When
reaction was complete the cooled mixture was diluted with water and extracted with chloroform. The extract was
dried over calcium chloride. Solvent and excess of anisole were distilled off, and the residue was vacuum-distilled.
Redistillation gave 48 g (74%) of a fraction having b.p. 118-119° (5 mm), n_D^{20} 1.5486 and d_4^{20} 1.2307;

Found   MR 56.08
$C_{10}H_{10}OCl_2$ $|_4$.   Calculated   MR 55.69
Found %: C 55.34; 55.54; H 4.74; 4.75; Cl 32.69; 32.54
$C_{10}H_{10}OCl_2$.   Calculated %: C 55.32;   H 4.61;   Cl 32.67

Oxidation of the product with a 5% alkaline solution of potassium permanganate gave a 90% yield of p-anisic
acid, m.p. 184.5°.

Found %: C 63.42; 63.56; H 5.39; 5.41
$C_8H_8O_3$.   Calculated %: C 63.15;   H 5.30

For p-anisic acid the literature [5] gives m.p. 184.5°.

Condensation of Phenol with 3,3,3-Trichloropropene. A mixture of 66 g (0.45 mole) of 3,3,3-trichloropropene
220 g (2.34 moles) of freshly distilled phenol, and 4 g of aluminum chloride was heated in a boiling water bath for
four hours. The mixture was cooled, diluted with water, and extracted with chloroform. The chloroform extract was
dried over calcium chloride. After solvent and unchanged original substances had been distilled off, 75 g of a sub-
stance distilling over the range 100-160° (5 mm) was obtained, together with 8 g of residue. Fractionation through a
40-cm column gave a fraction, amounting to 48 g (50%), having b.p. 116-117° (3 mm), n_D^{20} 1.5727; and d_4^{20} 1.3050.

Found   MR 51.25
$C_9H_8OCl_2$ $|_4$.   Calculated   MR 51.00
Found %: C 53.41; 53.29; H 4.10; 4.04; Cl 34.37; 34.38
$C_9H_8OCl_2$.   Calculated %: C 53.23;   H 3.97;   Cl 34.92

A second fraction, amounting to 21 g (22%), had b.p. 130-131° (3 mm), n_D^{20} 1.5732 and d_4^{20} 1.3057.

Found   MR 51.26
$C_9H_8OCl_2$ $|_4$.   Calculated   MR 51.00
Found %: C 53.44; 53.64; H 4.01; 4.01; Cl 34.89; 34.55
$C_9H_8Cl_2O$.   Calculated %: C 53.23;   H 3.97;   Cl 34.92

When allowed to stand, the substance solidified: m.p. 40.5-41° (from petroleum ether).

The lower-boiling compound was o-(3,3-dichloroallyl)phenol, and the higher-boiling compound was the corresponding p-substituted phenol.

When the reaction between phenol and 3,3,3-trichloropropene was carried out in absence of aluminum chloride, but otherwise under the same conditions, the same products were obtained, but the total yield was only 50%.

Methylation of the Products of the Condensation of Phenol with 3,3,3-Trichloropropene. The substance boiling at 116° (3 mm) obtained in the previous experiment was methylated with the equivalent amount of dimethyl sulfate, and a compound having b.p. 109° (4.5 mm), n_D^{20} 1.5525 and d_4^{20} 1.2372, was obtained in almost quantitative yield.

$$C_{10}H_{10}OCl_2F_4.$$
Found   MR 56.13
Calculated   MR 55.69
Found%: C 55.13; 55.02; H 4.69; 4.50; Cl 32.57; 32.18

$$C_{10}H_{10}OCl_2.$$
Calculated%: C 55.32   H 4.61;   Cl 32.67

Oxidation of this compound with alkaline potassium permanganate gave an 85% yield of o-anisic acid, m.p. 98.5°.

$$C_8H_8O_3.$$
Found %: C 63.08; 63.00; H 5.27; 5.44
Calculated%: C 63.15;   H 5.30

For o-anisic acid the literature [6] gives m.p. 98.5°.

Methylation of the second isomer, b.p. 130° (3 mm), yielded a methoxy compound identical in its constants with the 1,1-dichloro-3-p-methoxyphenylpropene obtained by the condensation of anisole with 3,3,3-trichloropropene. A mixture melting point test on the anisic acids obtained from the two samples of dichloro(methoxyphenyl)propene showed no depression.

Reaction of Sodium Phenoxide with 3,3,3-Trichloropropene. A solution of 1 mole of phenol, 1 mole of caustic soda, and 0.25 mole of 3,3,3-trichloropropene in 100 ml of ethanol was heated in a boiling water bath for six hours. The reaction mixture was diluted with water, and excess of aqueous caustic soda was added. The mixture was extracted with ether, and the ether extract was dried over calcium chloride. Solvent was distilled off, and the residue yielded 12 g of a neutral substance, probably consisting of 1,1-dichloro-3-phenoxypropene, b.p. 103-104° (7 mm); n_D^{20} 1.5534; d_4^{20} 1.2718.

Found %: C 52.90; 53.07; H 3.69; 3.79; Cl 34.85
Calculated%: C 53.23;   H 3.97;   Cl 34.92
Found   MR 51.13
$$C_9H_8OCl_2.$$
Calculated   MR 51.12

Acidification of the alkaline solution yielded 16 g of an oil, which was found to be a mixture of two isomers of (3,3-dichloroallyl)phenol.

Hydrolysis of 1,1-Dichloro-3-p-methoxyphenylpropene. A mixture of 10 g of p-CH₃OC₆H₄CH₂CH = CCl₂ and 30 g of 90% sulfuric acid was heated at 100-110° until hydrogen chloride ceased to be evolved (20 minutes). The reaction mixture was poured into water and treated with excess of barium carbonate. The precipitate of barium sulfate was filtered off, and the mother liquor was evaporated until crystallization began, when precipitation was effected by addition of alcohol. The barium sulfonate that separated was purified by reprecipitation from water with alcohol and was then dried over phosphoric oxide in a vacuum. The yield was about 90%.

Found %: C 36.16; 36.98; H 3.53; 3.41; S 9.70; 9.86
Ba[SO₃C₆H₃(OCH₃)CH₂CH₂COOH]₂ Calculated% C 36.62;   H 3.38;   S 9.78

Hydrolysis of 1,1-Dichloro-3-phenylpropene. The hydrolysis of 52 g of C₆H₅CH₂CH = CCl₂ was effected with 180 g of 92% sulfuric acid at 55-60° for 20-30 minutes. When the reaction mixture was set aside in the cold overnight, crystals of free sulfonic acid were precipitated in 95% yield. The pure sulfohydrocinnamic acid was obtained by passing an aqueous solution of its barium salt through a cationite and then evaporating the solution and vacuum-drying the product in a Fischer pistol heated by methanol vapor. The product formed colorless hygroscopic crystals that rapidly darkened.

Found %: C 43.09; 43.18; H 4.77;
4.71; S 12.62 12.55
C₆H₄(SO₃H)CH₂CH₂CO₂H · H₂O.   Calculated%: C 43.54; H 4.87; S 12.92

SUMMARY

1. A study was made of the condensation of 3,3,3-trichloropropene with bromobenzene, chlorobenzene, and anisole, and the following previously unknown compounds were isolated in the pure state: p-$BrC_6H_4CH_2CH = CCl_2$; p-$ClC_6H_4CH_2CH = CCl_2$; p-$CH_3OC_6H_4CH_2CH = CCl_2$.

2. It was found that, when 3,3,3-trichloropropene reacts with phenol in presence or absence of aluminum chloride, a mixture of $HOC_6H_4CH_2CH = CCl_2$ and p-$HOC_6H_4CH_2CH = CCl_2$ is formed. When the condensation is carried out with sodium phenoxide in an alcoholic medium, not only the above-mentioned ortho and para isomers are formed, but also the phenoxy derivative $C_6H_5OCH_2CH = CCl_2$.

3. It was shown that 1,1-dichloro-3-p-chlorophenylpropene and 3-p-bromophenyl-1,1-dichloropropene unite with chlorine with formation of p-$ClC_6H_4CH_2CHCl \cdot CCl_3$ and p-$BrC_6H_4CH_2CHClCCl_3$.

4. A study was made of the hydrolysis of the following compounds by concentrated H_2SO_4: p-$ClC_6H_4CH_2CH \cdot CCl_2$; p-$BrC_6H_4CH_2CH = CCl_2$; p-$CH_3OC_6H_4CCH_2H = CCl_2$ and $C_6H_5CH_2CH = CCl_2$. It was found that the first two compounds are converted smoothly into the corresponding halohydrocinnamic acids; the other two compounds are not only hydrolyzed at the dichlorovinyl group, but are also sulfonated in the benzene ring.

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DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 13. DIESTERS OF 2-(2-ALKOXYETHOXY)VINYLPHOSPHONO-MONO-,DI-, AND -TRI-THIOIC ACIDS

K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov

This paper describes the preparation and some of the properties of diester of 2-(2-alkoxyethoxy)vinylphosphono-mono-, -di-, and -tri-thioic acids. The information in the literature on such esters is very limited. We have found a simple and readily accessible method for the synthesis of 2-alkoxy- and 2-phenoxy-vinylphosphonothioic dichlorides and 2-(2-alkoxyethoxy)vinylphosphonothioic dichlorides by the action of hydrogen sulfide on the product of the addition of phosphorus pentachloride to a vinyl ether [1].

The phosphonothioic dichlorides being readily accessible, we decided to prepare derivatives of these (esters and thio esters) by the reactions:

$$ROCH_2-CH_2-O-CH=CHPOCl_2 + 2NaSR = ROCH_2-CH_2-O-CH=CHPO(SR)_2 + 2NaCl. \quad (1)$$
$$ROCH_2-CH_2-O-CH=CHPSCl_2 + 2NaOR = ROCH_2-CH_2-O-CH=CHPS(OR)_2 + 2NaCl. \quad (2)$$
$$ROCH_2-CH_2-O-CH=CHPSCl_2 + 2NaSR = ROCH_2-CH_2-O-CH=CHPS(SR)_2 + 2NaCl. \quad (3)$$
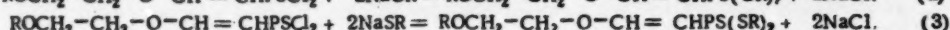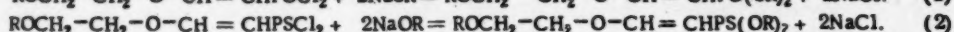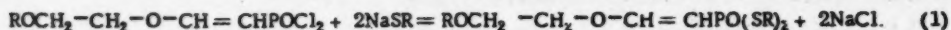
In this way we prepared S,S-diethyl 2-(2-methoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonodithioates, O,O-dimethyl and O,O-diethyl 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonothioates, and diethyl 2-(2-methoxyethoxy)- and 2-(2-ethoxyethoxy)-vinylphosphonotrithioates. The constants of these compounds are given in the table.

Diesters of 2-(2-alkoxyethoxy)vinylphosphono-mono-, -di-, and -tri-thioic acids are liquids of somewhat unpleasant odor, soluble in all organic solvents, and distillable only under reduced pressure.

EXPERIMENTAL

O,O-Dimethyl 2-(2-Methoxyethoxy)vinylphosphonothioate $CH_3OCH_2CH_2OCH=CHPS(OCH_3)_2$. Sodium methoxide was prepared in a three-necked flask fitted with stirrer and reflux condenser from 40 ml of absolute methanol and 2.3 g of sodium, and it was stirred and cooled with ice water while 10.85 g of 2-(2-methoxyethoxy)vinylphosphonothioic dichloride was added gradually. The reaction mixture was then diluted with 100 ml of absolute ether and set aside overnight. On the next day the mixture was heated for two hours in a water bath at 35°; the ether layer was then removed, and the precipitate present was washed several times with ether. Vacuum fractionation gave a product amounting to 6.5 g (58%), having b.p. 119° (2 mm); n_D^{20} 1.4775; d_4^{20} 1.1624.
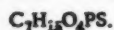
$$\text{Found \%:} \quad P \ 13.64; \ 13.63$$
$$C_7H_{15}O_4PS. \qquad \text{Calculated \%:} \quad P \ 13.71$$

O,O-Diethyl 2-(2-Methoxyethoxy)vinylphosphonothioate $CH_3OCH_2CH_2OCH=CHPS(OC_2H_5)_2$. 2-(2-Methoxyethoxy)vinylphosphonothioic dichloride (11.85 g) was added with cooling and slow stirring to sodium ethoxide prepared from 2.3 g of sodium and 60 ml of absolute ethanol. When reaction was complete, the mixture was diluted with 120 ml of absolute ether and set aside overnight. On the next day the mixture was warmed in a water bath and the ether layer was poured off, the precipitate being washed several times with ether. Drying over sodium sulfate, followed by vacuum fractionation, yielded 10 g (73.5%) of a substance having b.p. 120° (1 mm); n_D^{20} 1.4760; d_4^{20} 1.0904.
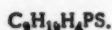
$$\text{Found \%: P } 12.19; \ 12.13$$
$$C_9H_{19}H_4PS. \qquad \text{Calculated \%: P } 12.20$$

O,O-Dimethyl 2-(2-Ethoxyethoxy)vinylphosphonothioate $C_2H_5OCH_2CH_2OCH=CHPS(OCH_3)_2$. 2-(2-Ethoxyethoxy)vinylphosphonothioic dichloride (12.45 g) was added gradually with cooling and stirring to sodium methoxide prepared

TABLE

Formula	B.p. °C (p in mm)	n_D^{20}	d_4^{20}	Yield (%)
$CH_3-O-CH_2-CH_2-O-CH=CHPO(SC_2H_5)_2$	150/1	1.5511	1.1435	80
$n-C_4H_9-O-CH_2-CH_2-O-CH=CHPO(SC_2H_5)_2$	186/2	1.5365	1.1180	87
$CH_3-O-CH_2-CH_2-O-CH=CHPS(OCH_3)_2$	119/6	1.4775	1.1024	58
$CH_3-O-CH_2-CH_2-O-CH=CHPS(OC_2H_5)_2$	120/1	1.4760	1.0904	73
$C_2H_5-O-CH_2-CH_2-O-CH=CHPS(OCH_3)_2$	127/2	1.4712	1.1321	78
$C_2H_5-O-CH_2-CH_2-O-CH=CHPS(OC_2H_5)_2$	133/2	1.4695	1.0781	82
$n-C_4H_9-O-CH_2-CH_2-O-CH=CHPS(OCH_3)_2$	141/1	1.4690	1.0922	83
$n-C_4H_9-O-CH_2-CH_2-O-CH=CHPS(OC_2H_5)_2$	145/1	1.4680	1.0296	80
$CH_3-O-CH_2-CH_2-O-CH=CHPS(SC_2H_5)_2$	157/2	1.5890	1.1579	75
$C_2H_5-O-CH_2-CH_2-O-CH=CHPS(SC_2H_5)_2$	176/2	1.5745	1.1417	83

from 2.3 g of sodium and 50 ml of absolute methanol. When the addition was complete, the mixture was diluted with 100 ml of ether. On the next day treatment as described above yielded 9.7 g (78%) of a substance having b.p. 127° (2 mm); n_D^{20} 1.4712; d_4^{20} 1.1321.

$$\text{Found \%: P 12.95; 12.84}$$
$$C_8H_{17}O_4PS. \qquad \text{Calculated \%: P 12.84}$$

O,O-Diethyl 2-(2-Ethoxyethoxy)vinylphosphonothioate $C_2H_5OCH_2CH_2OCH=CHPS(OC_2H_5)_2$. 2-(2-Ethoxy-ethoxy)vinylphosphonothioic dichloride (12.45 g) was added gradually with cooling and stirring to sodium ethoxide prepared from 2.3 g of sodium and 50 ml of absolute ethanol. When the addition was complete, the reaction mixture was diluted with 100 ml of ether and set aside overnight. On the next day the ether layer was poured off and the precipitate was washed several times with ether. Fractional distillation under reduced pressure yielded 11.4 g (82%) of a substance having b.p. 133° (2 mm); n_D^{20} 1.4695; d_4^{20} 1.0781.

$$\text{Found \%: P 10.15; 10.14}$$
$$C_{10}H_{21}O_4PS. \qquad \text{Calculated \%: P 10.10}$$

O,O-Dimethyl 2-(2-3utoxyethoxy)vinylphosphonothioate $n-C_4H_9OCH_2CH_2OCH=CHPS(OCH_3)_2$. 2-(2--Butoxyethoxy)vinylphosphonothioic dichloride (8g) was added gradually with stirring and cooling to sodium methoxide prepared from 50 ml of absolute methanol and 1.3 g of sodium. When reaction was complete, the mixture was diluted with 110 ml of absolute ether. On the next day the mixture was warmed in a water bath for two hours, the ether layer was poured off, and the precipitate was washed repeatedly with ether. The ether solution of the reaction mixture was dried over sodium sulfate. Fractionation then gave 6.5 g (83%) of a substance with b.p.141° (1 mm); n_D^{20} 1.4690; d_4^{20} 1.0922.

$$\text{Found \%: P 10.77; 10.95}$$
$$C_{10}H_{21}O_4P. \qquad \text{Calculated \%: P 11.19}$$

O,O-Diethyl 2-(2-Butoxyethoxy)vinylphosphonothioate $n-C_4H_9OCH_2CH_2OCH=CHPS(OC_2H_5)_2$. 2-(2-Butoxyeth-oxy) vinylphosphonothioic dichloride(18.9 g) was added with stirring to sodium ethoxide prepared from 60 ml of absolute ethanol and 2.3 g of sodium. When the addition was complete, the mixture was diluted with 120 ml of absolute ether. On the next day the above-described operations yielded 17 g (80%) of a substance having b.p. 145° (1 mm) n_D^{20} 1.4680; d_4^{20} 1.0296.

$$\text{Found \%: P 10.51; 10.32}$$
$$C_{12}H_{25}O_4PS. \qquad \text{Calculated \%: P 10.47}$$

S,S-Diethyl 2-(2-Methoxyethoxy)vinylphosphonodithioate $CH_3OCH_2CH_2OCH=CHPO(SC_2H_5)_2$. Sodium (2.3 g), finely dispersed for reaction by the Brühl method, was added to absolute ether contained in a three-necked flask fitted with stirrer and reflux condenser. The mixture was cooled with ice and salt and was stirred slowly while dropwise addition of 8 g of ethanethiol was made. On the next day the resulting sodium mercaptide was warmed in a water bath 35°, and was then cooled again and stirred while 10.95 g of 2-(2-methoxyethoxy)vinylphosphonic dichloride was added. The mixture was then left overnight. On the next day it was heated in a water bath at 35° for 2 hours 30 minutes, the ether layer was poured off, and the precipitate was repeatedly washed with ether. The ethereal filtrate, dried over sodium sulfate and fractionated, yielded 10 g (80%) of a substance having b.p. 150° (1 mm); n_D^{20} 1.5511; d_4^{20} 1.1435.

$$\text{Found \%: P 11.49; 11.49}$$
$$C_9H_{19}O_3PS_2. \qquad \text{Calculated \%: P 11.48}$$

S,S-Diethyl 2-(2-Butoxyethoxy)vinylphosphonodithioate $n-C_4H_9OCH_2CH_2OCH=CHPO(SC_2H_5)_2$. 2-(2-Butoxy-ethoxy)vinylphosphonic dichloride (12 g) was added gradually with stirring to sodium ethylmercaptide prepared in ab-

solute ether from 2.3 g of finely dispersed sodium and 8 g of ethanethiol. The product, amounting to 12.5 g (87%), had b. p. 186° (2 mm); n_D^{20} 1.5365; d_4^{20} 1.1180.

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Found %: P 9.82; 9.91

$C_{12}H_{25}O_3PS_2$.   Calculated %: P 9.93

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Diethyl 2-(2-Methoxyethoxy) vinylphosphonotrithioate $CH_3OCH_2CH_2OCH = CHPS(SC_2H_5)_2$. Ethanethiol (9 g) was added gradually with stirring to an ice-cooled mixture of 2.3 g of Brühl sodium and absolute ether contained in a three-necked flask fitted with stirrer. On the next day 11.75 g of 2-(2-methoxyethoxy) vinyl-phosphonothioic dichloride was added with stirring to the sodium ethylmercaptide. Treatment of the reaction mixture in the way described above yielded 11 g (75%) of a substance having b. p. 157° (2 mm); n_D^{20} 1.5890; d_4^{20} 1.1579.

<div align="center">

Found %: P 10.87; 10.88

$C_9H_{19}O_3PS_3$ Calculated %: P 10.83

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Diethyl 2-(2-Ethoxyethoxy) vinylphosphonotrithioate $C_2H_5OCH_2CH_2OCH = CHPS(SH_2H_5)_2$. 2-(2-Ethoxlyethoxy)vinylphosphonothioic dichloride (12.45 g) was added gradually to sodium mercaptide prepared from 9 g of ethanethiol and 2.3 g of finely dispersed sodium in a medium of absolute ether. On the next day the mixture was warmed for two hours in a water bath at 35°, the ether layer was poured off, and the precipitate was washed repeatedly with ether. The ether filtrate, dried over sodium sulfate and fractionated, yielded 12.5 g (83%) of a substance having b. p. 176° (1 mm); n_D^{20} 1.5745; d_4^{20} 1.1417.

<div align="center">

Found %: P 10.44; 10.46

$C_{10}H_{21}O_2P_3$.   Calculated %: P 10.33

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SUMMARY

1. Reaction of 2-(2-alkoxyethoxy) vinylphosphonothioic dichlorides with sodium methoxide and ethoxide yielded 0.0-dimethyl and 0.0-diethyl esters of 2-(2-methoxyethoxy)-, 2-(2-ethoxyethoxy)- and 2-(2-butoxy-ethoxy)-vinylphosphonothioic acids.

2. Reaction of 2-(2-alkoxyethoxy)vinylphosphonic and 2-(2-alkoxyethoxy)vinylphosphonothioic di-chlorides with sodium ethylmercaptide yielded S,S-diethyl 2-(2-methoxyethoxy)- and 2-(2-butoxyethoxy)-vinylphosphonothioates and diethyl 2-(2-methoxyethoxy)- and 2-(2-ethoxyethoxy)-vinylphosphonotrithioates.

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* T. p. = C. B. Translation pagination.

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 14. DIESTERS OF STYRYLPHOSPHONIC ACID

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We have previously described diesters of 2-alkoxy- and 2-phenoxy-vinylphosphonic acids [1-3]. In the present paper we report the synthesis and some of the properties of diesters of styrylphosphonic acid (i.e. 2-phenylvinylphosphonic acid). The syntheses of these compounds were effected by the action of alcohols on styrylphosphonic dichloride, which we were the first to prepare and characterize [4]. Dimethyl styrylphosphonate is a white crystalline substance (m.p. 41-42°), soluble in many organic solvents and in water. The other esters are clear oily liquids of characteristic odor, soluble in the usual organic solvents, but not in water. The properties of the compounds obtained are given in the table.

EXPERIMENTAL

Dimethyl Styrylphosphonate $C_6H_5OCH = CHPO(OCH_3)_2$. A mixture of 3.2 g of absolute methanol, 7.9 g of pyridine, and 40 ml of dry benzene was prepared in a three-necked flask fitted with stirrer, reflux condenser protected with a calcium chloride tube, and a dropping funnel. With good cooling and stirring, a solution of 11.05 g of styrylphosphonic dichloride in 15 ml of benzene was added. When the whole of the acid chloride had been added, the reaction mixture was heated for two hours in a water bath, after which pyridine hydrochloride was filtered off and the filtrate was washed with saturated sodium carbonate solution and dried over calcined sodium sulfate. On the next day benzene was distilled from the filtrate and the residue was vacuum-distilled. Three fractionations yielded 6 g (57%) of dimethyl styrylphosphonate, b.p. 129° (2 mm), m.p. 41-42°.

$$C_{10}H_{13}O_3P.$$

Found %: C 56.42; 56.57; H 6.10; 6.20
Calculated %: C 56.60; H 6 13

All of the following styrylphosphonic esters were synthesized by the method described for the dimethyl ester.

Diethyl Styrylphosphonate $C_6H_5OCH = CHPO(OC_2H_5)_2$. Styrylphosphonic dichloride (11.05 g) was added to 4.6 g of ethanol and 7.9 g of pyridine, and the product was 8 g (67%) of diethyl styrylphosphonate, b.p. 138° (2 mm) d_4^{20} 1.1082; n_D^{20} 1.5325.

$$C_{12}H_{17}O_3P.$$

Found %: C 60.11; 60.09; H 7.25; 7.28
Calculated %: C 60.00; H 7.08

Dipropyl Styrylphosphonate $C_6H_5CH = CHPO(OC_3H_7-n)_2$. Styrylphosphonic dichloride (11.05 g) was added to 6 g of propyl alcohol and 7.9 g of pyridine, and the product was 10 g (75%) of dipropyl styrylphosphonate, b.p. 158° (2 mm); d_4^{20} 1.0700; n_D^{20} 1.5230.

$$C_{14}H_{21}O_3P.$$

Found %: C 62.82; 62.98; H 8.08; 8.11
Calculated %: C 62.67; H 7.83

Diisopropyl Styrylphosphonate $C_6H_5CH = CHPO(OC_3H_7-i)_2$. With respect to the conditions and the amounts of the reactants, the procedure was precisely analogous to that used for the dipropyl ester. The product was 3.5 g (26%) of diisopropyl styrylphosphonate, b.p. 137° (1 mm); d_4^{20} 1.0547; n_D^{20} 1.5164.

$$C_{14}H_{21}O_3P.$$

Found %: C 62.81; 63.03; H 7.90; 7.78
Calculated %: C 62.67; H 7.83

Dibutyl Styrylphosphonate $C_6H_5CH = CHPO(OC_4H_9-n)_2$. Styrylphosphonic dichloride (11.05 g) was added to 7.4 g of butyl alcohol and 7.9 g of pyridine, and the product was 12 g (81%) of a substance having b.p. 172° (2 mm);

TABLE

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_6H_5-CH=CHPO(OCH_3)_2$	129 (2), 41 - 42		
$C_6H_5-CH=CHPO(OC_2H_5)_2$	138 (2)	1.5325	1.1082
$C_6H_5-CH=CHPO(OC_3H_7-n)_2$	158 (2)	1.5230	1.0700
$C_6H_5-CH=CHPO(OC_3H_7-i)_2$	137 (1)	1.5164	1.0547
$C_6H_5-CH=CHPO(OC_4H_9-n)_2$	172-173 (2)	1.5153	1.0403
$C_6H_5-CH=CHPO(OC_4H_9-i)_2$	159 (2)	1.5130	1.0342
$C_6H_5-CH=CHPO(OC_3H_5)_2$	159 (2)	1.5445	1.1076
$C_6H_5-CH=CHPO(OC_6H_{13}-n)_2$	187.5 (2)	1.5500	1.0054
$C_6H_5-CH=CHPO(OC_7H_{15}-n)_2$	213 (2)	1.5020	0.9888
$C_6H_5-CH=CHPO(OCH_2-CH_2-O-CH_3)_2$	176 (2)	1.5246	1.1501
$C_6H_5-CH=CHPO(OCH_2-CH_2-O-C_2H_5)_2$	187 (2)	1.5179	1.1114

d_4^{20} 1.0403; n_D^{25} 1.5153.

	Found %. C 64.81; 64.78; H 8.52; 8.48
$C_{16}H_{25}O_3P.$	Calculated%: C 64.86; H 8.44

Diisobutyl Styrylphosphonate $C_6H_5CH=CHPO(OC_4H_9-i)_2$. This was prepared under the same conditions as those used for the dibutyl ester. The yield of diisobutyl styrylphosphonate was 10 g (67%), and it had b.p. 159° (2 mm) n_D^{20} 1.5130; d_4^{20} 1.0342.

	Found %. C 64.47; 64.46; H 8.32; 8.26
$C_{16}H_{25}O_3P.$	Calculated %: C 64.86; H 8.44

Diallyl Styrylphosphonate $C_6H_5CH=CHPO(OC_3H_5)_2$. Styrylphosphonic dichloride (22.1 g) was added to 11.62 g of allyl alcohol and 15.8 g of pyridine, and the product was 15 g (56%) of diallyl styrylphosphonate, b.p. 159° (2 mm) d_4^{20} 1.1076; n_D^{20} 1.5445.

	Found %. C 63.53; 63.48; H 6.71; 3.50
$C_{14}H_{17}O_3P.$	Calculated%: C 63.63; H 6.43

Dihexyl Styrylphosphonate $C_6H_5CH=CHPO(OC_6H_{13}-n)_2$. Styrylphosphonic dichloride (11.05 g) was added to 10.21 g of hexyl alcohol and 7.9 g of pyridine. The substance isolated had b.p. 187.5° (2 mm); d_4^{20} 1.0054; n_D^{20} 1.5500.

	Found%. C 68.00; 68.12; H 9.71; 9.60
$C_{20}H_{33}O_3P.$	Calculated%: C 68.18; H 9.37

Diheptyl Styrylphosphonate $C_6H_5-CH=CHPO(OC_7H_{15}-n)_2$. Styrylphosphonic dichloride (22.1 g) was added to 23.2 g of absolute heptyl alcohol and 15.8 g of pyridine. The substance isolated, amounting to 9.2 g (65%), had b.p. 213° (1 mm); n_D^{20} 1.5020; d_4^{20} 0.9888.

	Found %. P 7.82; 7.93
$C_{22}H_3O_2P$	Calculated%: P 8.01

Bis(2-methoxyethyl)Styrylphosphonate $C_6H_5-CH=CHPO(OCH_2CH_2OCH_3)_2$. Styrylphosphonic dichloride (22.1 g) was added to 15.2 g of 2-methoxyethanol and 15.8 g of pyridine. The substance isolated (20 g) had b.p. 176° (2 mm); d_4^{20} 1.1501; n_D^{20} 1.5246.

	Found %. P 10.38; 10.17
$C_{14}H_{21}O_5P.$	Calculated%: P 10.33

Bis(2-ethoxyethyl) Styrylphosphonate $C_6H_5-CH=CHPO(OCH_2-CH_2-OC_2H_5)_2$. Styrylphosphonic dichloride (22.1 g) was added to 18 g of 2-ethoxyethanol and 15.8 g of pyridine. Fractionation yielded 21 g of ester, b.p. 187° (2 mm); d_4^{20} 1.1114; n_D^{20} 1.5179.

	Found %: C 58.28; 58.17; H 7.63; 7.43
$C_{16}H_{25}O_5P.$	Calculated%: C 58.53; H 7.62

SUMMARY

Eleven diesters of styrylphosphonic acid were prepared and characterized.

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• T.p. = C. B. Translation pagination.

DERIVATIVES OF UNSATURATED PHOSPHONIC ACIDS

COMMUNICATION 15. DIESTERS OF β-CHLOROSTYRYLPHOSPHONIC AND PHENYLETHYNYLPHOSPHONIC ACIDS

K. N. Anisimov and A. N. Nesmeyanov

β-Chlorostyrylphosphonic dichloride reacts with alcohols in presence of pyridine in the same manner as all acid chlorides of unsaturated phosphonic acids [1], i.e. with formation of diesters of β-chlorostyrylphosphonic acid together with pyridine hydrochloride. By this method we have prepared the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, and diallyl esters of β-chlorostyrylphosphonic acid.

Dimethyl β-chlorostyrylphosphonate has been prepared previously by Bergman and Bondi [2] by reaction between methyl iodide and silver S-chlorostyrylphosphonate; these authors report only the boiling point of the compound.

All of the esters synthesized are viscous liquids, soluble in organic solvents. They are stable to storage, with the exception of diisopropyl β-chlorostyrylphosphonate, and this decomposes partially when vacuum-distilled and polymerizes in the flask. All the other esters can be vacuum-distilled without decomposition. Physical constants of the compounds obtained are given in Table 1.

For dimethyl β-chlorostyrylphosphonate, Bergman and Bondi [2] give b.p. 202-203° (14 mm).

The values of the boiling points, densities, and refractive indices of diesters of β-chlorostyrylphosphonic acid are higher than those of the corresponding diesters of styrylphosphonic acid. When diethyl or diisobutyl β-chlorostyrylphosphonate was treated with the calculated amount of alcoholic potash in the cold, potassium chloride was precipitated, and the corresponding ester of phenylethynylphosphonic acid was formed. Diethyl and diisobutyl phenylethynylphosphonates are clear liquids, insoluble in water, but soluble in many organic solvents. Their physical constants are given in Table 2.

EXPERIMENTAL

Dimethyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OCH_3)_2$. A mixture of 3.2 g of absolute methanol, 7.9 g of pyridine, and 50 ml of benzene was prepared in a three-necked flask fitted with stirrer, reflux condenser protected with a calcium chloride tube, and dropping funnel. With good cooling and stirring, dropwise addition was made of a solution of 12.77 g of β-chlorostyrylphosphonic dichloride in 15 ml of benzene. On the next day the reaction mixture was heated for two hours in a water bath. Pyridine hydrochloride was then filtered off, and the filtrate was washed three times with saturated sodium carbonate solution and dried over calcined sodium sulfate. On the next day benzene was distilled from the filtrate, and the residue was vacuum-distilled. Three fractionations yielded 6 g (48%) of dimethyl β-chlorostyrylphosphonate, b.p. 148-149° (1 mm); d_4^{20} 1.2812; n_D^{20} 1.5595.

$$C_{10}H_{12}O_3PCl.$$
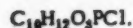
Found %: C 49.04; 48.86; H 5.39; 5.34
Calculated %: C 48.68; H 4.86

The other β-chlorostyrylphosphonic esters were synthesized by the method described above.

Diethyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_2H_5)_2$. β-Chlorostyrylphosphonic dichloride (12.77 g) was added to 4.6 g of absolute ethanol and 7.9 g of pyridine. The product was 9 g (65%) of diethyl β-chlorostyrylphosphonate, b.p. 159° (2 mm); d_4^{20} 1.2070; n_D^{20} 1.5410.

$$C_{12}H_{16}O_3ClP.$$
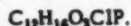
Found %: C 52.52; 52.43; H 6.06; 5.95
Calculated %: C 52.45; H 5.82

Diallyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_3H_5)_2$. β-Chlorostyrylphosphonic dichloride (12.77 g) was added to 5.8 g of allyl alcohol and 7.9 g of pyridine. The product was 8 g (53%) of diallyl β-chlorostyrylphosphonate, b.p. 164-165° (1 mm); d_4^{20} 1.1920; n_D^{20} 1.5504.
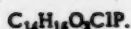
<div align="right">
Found %: C 56.00; 56.15; H 5.11; 5.17
</div>

$C_{14}H_{16}O_3ClP.$ Calculated%: C 56.27;   H 5.36

Dipropyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_3H_7-n)_2.$ β-Chlorostyrylphosphonic dichloride (12.77 g) was added gradually to 6 g of propyl alcohol. The reaction was carried out in presence of 8 g of pyridine in a benzene medium. The product was 10 g (66%) of dipropyl β-chlorostyrylphosphonate, b.p. 166° (2 mm); d_4^{20} 1.1584; n_D^{20} 1.5288.
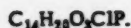
<div align="right">
Found %: C 55.29; 55.26; H 6.65; 6.72
</div>

$C_{14}H_{20}O_3ClP.$ Calculated%: C 55.53;   H 6.61

TABLE 1

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_6H_5CCl = CHPO(OCH_3)_2$	148−149 (1)	1.5595	1.2812
$C_6H_5CCl = CHPO(OC_2H_5)_2$	159 (2)	1.5410	1.2070
$C_6H_5-CCl = CHPO(OC_3H_7-n)_2$	166 (2)	1.5288	1.1584
$C_6H_5-CCl = CHPO(OC_3H_7-i)_2$	149 (1)	1.5220	1.1424
$C_6H_5-CCl = CHPO(OC_4H_9-n)_2$	176 (1)	1.5212	1.1202
$C_6H_5-CCl = CHPO(OC_4H_9-i)_2$	165 (1)	1.5188	1.1168
$C_6H_5-CCl = CHPO(OC_5H_6)_2$	164−165 (1)	1.5504	1.1920

TABLE 2

Formula	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}
$C_6H_5C \equiv CPO(OC_2H_5)_2$	155 (1)	1.5312	1.1500
$C_6H_5C \equiv CPO(OC_4H_9-i)_2$	159−161 (1)	1.5090	1.0423

Diisopropyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_3H_7-i)_2.$ To 6 g of isopropyl alcohol and 7.9 g of pyridine, 12.77 g of β-chlorostyrylphosphonic dichloride was added. The product was 3 g of diisopropyl β-chlorostyrylphosphonate, b.p. 149° (1 mm); d_4^{20} 1.1424; n_D^{20} 1.5220.
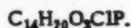
<div align="right">
Found %: C 55.68; 55.78; H 6.65; 6.88
</div>

$C_{14}H_{20}O_3ClP.$ Calculated%: C 55.53;   H 6.61

Dibutyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_4H_9-n)_2.$ β-Chlorostyrylphosphonic dichloride (12.77 g) was added to 4.7 g of butyl alcohol.   The reaction was carried out in presence of 7.9 g of pyridine in a benzene medium. The product was 12 g (81%) of dibutyl β-chlorostyrylphosphonate, b.p. 176° (1 mm); d_4^{20} 1.1202; n_D^{20} 1.5212
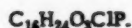
<div align="right">
Found %: C 57.89; 58.18; H 7.40; 7.34
</div>

$C_{16}H_{24}O_3ClP.$ Calculated%: C 58.09;   H 7.26

Diisobutyl β-Chlorostyrylphosphonate $C_6H_5CCl = CHPO(OC_4H_9-i)_2.$ This was prepared under the same conditions as those used for the preparation of the dibutyl ester. The yield of diisobutyl β-chlorostyrylphosphonate was 10 g (60%), and it had b.p. 165° (1 mm); d_4^{20} 1.1168; n_D^{20} 1.5188.
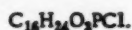
<div align="right">
Found %: C 57.96; 57.80; H 7.24; 70.2
</div>

$C_{16}H_{24}O_3PCl.$ Calculated%: C 58.09;   H 7.26

Diethyl Phenylethynylphosphonate $C_6H_5C \equiv CPO(OC_2H_5)_2$ Diethyl β-chlorostyrylphosphonate (3.82 g) was added to a solution of 0.77 g of caustic potash in alcohol. The solution immediately became warm, and potassium chloride was precipitated. The reaction mixture was heated for one hour in a water bath, and the precipitate was filtered off. Alcohol was distilled from the filtrate, and vacuum distillation of the residue yielded 2.6 g of a substance having b.p. 155° (1 mm); n_D^{20} 1.5312; d_4^{20} 1.1500.

<div align="right">
Found %: P 13.00; 12.96
</div>
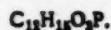
$C_{12}H_{15}O_3P.$ Calculated%: P 13.02

Diisobutyl Phenylethynylphosphonate $C_6H_5C \equiv CPO(OC_4H_9 -i)_2$. This was prepared similarly to the diethyl ester from 17.5 g of diisobutyl β-chlorostyrylphosphonate and 3.2 g of caustic potash. The product (10.8 g) had b.p. 159-161° (1 mm); n_D^{20} 1.5090; d_4^{20} 1.0423.

$$C_{15}H_{23}O_2P.$$

Found %: P 10.59; 10.57
Calculated %: P 10.54

SUMMARY

1. The diethyl, dipropyl, diisopropyl, dibutyl, diisobutyl, and diallyl esters of β-chlorostyrylphosphonic acid were prepared and characterized for the first time.

2. The diethyl and diisobutyl esters of phenylethynylphosphonic acid were prepared and characterized.

LITERATURE CITED

[1] K. N. Anisimov, N. E. Kolobova, and A. N. Nesmeyanov, Bull. Acad. Sci., USSR, Div. Chem. Sci., 1955, No. 2, 240 (T.p. 213)* .

[2] E. Bergman, A. Bondi, Ber. 66, 278 (1933).

* T.p. = C.B. Translation pagination.

ACTION OF SODIUM ON COMPOUNDS CONTAINING A $CCl_2 = CH$ GROUP

L. I. Zakharkin

Pinner [1, 2] was the first to investigate the action of sodium on the 2,2-dichlorovinyl group, the compound selected for study being 1,1-dichloropropene. He showed that, when the product of reaction between 1,1-dichloropropene and sodium was decomposed with water, propyne was formed in low yield [2]; treatment of the reaction product with carbon dioxide gave propiolic acid [3]. Pinner supposed that, in the reaction of 1,1-dichloropropene with sodium, the product had the composition $C_3H_4Cl_2Na_2$, the course of the reaction being as follows, with separation of sodium chloride only during the stage of decomposition with water:

$$CH_3CH = CCl_2 + 2Na \rightarrow C_3H_4Cl_2Na_2 \xrightarrow{H_2O} CH_3C \equiv CH + 2NaCl.$$
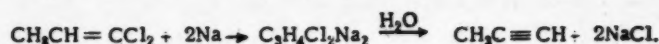
This reaction has not been studied further.

Various 2,2-dichlorovinyl derivatives now being readily available [4, 5], we considered that it was of interest to investigate this reaction from the preparative point of view, and also to elucidate the mechanism of the conversion of the $CCl_2 = CH$ group into the $HC \equiv C$ group, since we did not consider the mechanism postulated by Pinner to be very likely. We found, in agreement with previous work, that treatment of the product of reaction between 1,1-dichloro--1-pentene and sodium with carbon dioxide yielded 2-hexynoic acid, and that treatment of the product of reaction between 5,5-dichloro-N,N-diethyl-4-pentenylamine and sodium with benzaldehyde yielded 6-diethylamino-1-phenyl--2-hexyn-1-ol $C_6H_5CH(OH)C \equiv C-(CH_2)_3N(C_2H_5)_2$. These results show that the product of reaction between a 2,2--dichlorovinyl derivative and sodium contains $RC \equiv CNa$ and that this is formed by the removal of two chlorine atoms and one hydrogen atom from the $CCl_2 = CH$ group. It is to be expected that the chlorine will separate in the form of sodium chloride. It was found that only a very small amount of hydrogen was evolved in the reaction (2.5 % of the theoretical amount), and only when the reaction product was decomposed with water was the expected amount of hydrogen liberated (0.5 mole per mole of 2,2-dichlorovinyl derivative). It was found also that in this reaction it was necessary to take 4 g atoms of sodium for each mole of the 2,2-dichlorovinyl derivative, and not 2 g-atoms, as indicated by Pinner. These results can be explained on the assumption that hydrogen from the $CCl_2 = CH$ group becomes bound as sodium hydride, and the reaction of 2,2-dichlorovinyl derivative with sodium can be represented as follows:

$$RCH = CCl_2 + 4Na \rightarrow RC \equiv CNa + NaH + 2NaCl.$$

The formation of $RC \equiv CNa$ may proceed as follows:

$$RCH = CCl_2 + 2Na \longrightarrow \left[R-CH = C \begin{smallmatrix} Cl \\ \\ Na \end{smallmatrix} \right] \rightarrow RC \equiv CCl + NaH \xrightarrow{2 Na} RC \equiv CNa.$$
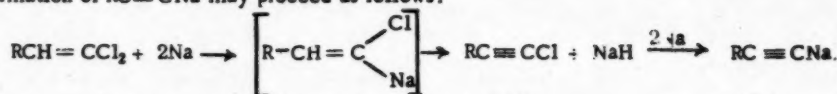
Confirmation of this reaction mechanism can be found in the formation of some monosubstituted acetylene and sodium or lithium hydride, which was observed in a number of cases when monohalo olefins of the type $RCH = CHX$ were treated with sodium or lithium [6, 7]. The replacement of chlorine by sodium in $RC \equiv C-Cl$ occurs very readily [8]. Our study of the action of sodium on 2,2-dichlorovinyl derivatives showed that the reaction proceeds fairly smoothly: in most of the cases investigated it gave the monosubstituted acetylene in a yield of 60-80 %.

The properties and yields of the monosubstituted acetylenes obtained are given in Table 1. In the case of β,β--dichlorostyrene we did not succeed in obtaining a good yield of ethynylbenzene owing to the impossibility of carrying out the reaction to completion. In the case of (3,3-dichloroallyl)benzene the product, obtained in satisfactory yield, was a mixture of substances —mainly phenylpropadiene. Taking 4,5,5-trichloro-N,N-diethyl-4-pentenylamine as our example, we showed that the $CCl_2 = CCl$ group is converted by sodium into the $HC \equiv C$ group:

$$(C_2H_5)_2N(CH_2)_3CCl = CCl_2 + 4Na \rightarrow (C_2H_5)_2N(CH_2)_3C \equiv CNa + 3NaCl.$$
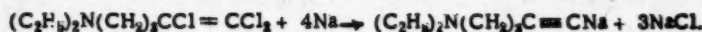
A good yield of N,N-diethyl-4-pentynylamine was obtained. Conversion of 5-ethoxy-1-pentyne into its organomagnesium bromide and treatment of the product with benzaldehyde gave a good yield of 6-ethoxy-1-phenyl-2-hexyn-1-ol.

EXPERIMENTAL

1,1-Dichloro-1-nonene. A mixture of 60 g of 1,1,1-trichlorononane and 3 g of anhydrous ferric chloride was heated at 60-75° until hydrogen chloride ceased to be evolved. The mixture was cooled, ferric chloride was filtered off, and the filtrate was diluted with chloroform and washed with hydrochloric acid. Fractionation through a column yielded 39.4 g (77.5%) of 1,1-dichloro-1-nonene, b.p. 85-86° (7 mm); n_D^{20} 1.4597; d_4^{20} 1.0106; found MR 52.84 Calculated MR 53.03.

	Found %:	C 55.21; 55.26;	H 8.02; 8.11
$C_9H_{16}Cl_2$.	Calculated %:	C 55.38;	H 8.20

1,1-Dichloro-5-ethoxy-1-pentene. A solution of 1-1-5-trichloro-1-pentene (40 g) and sodium ethoxide (from 6.5 g of sodium) in 85 ml of absolute alcohol was heated for four hours, cooled, and poured into water. The oil that separated was extracted with chloroform. Vacuum distillation yielded 29.3 g (69%) of 1,1-dichloro-5-ethoxy-1-pentene, b.p. 79-81° (11 mm); n_D^{20} 1.4642; d_4^{20} 1.1101; found MR 45.50; calculated MR 45 44.
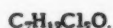
	Found %:	C 46.02; 45.8%;	H 6.75; 6.72
$C_7H_{12}Cl_2O$.	Calculated %:	C 45.90;	H 6.55

1,1-Dichloro-7-ethoxy-1-heptene. A solution of 1,1,7-trichloro-1-heptene (40 g) and sodium ethoxide (from 6 g of sodium) in 80 ml of absolute alcohol was heated for six hours. The product was 32.4 g (77%) of 1,1-dichloro--7-ethoxy-1-heptene, b.p. 114-115° (15 mm); n_D^{20} 1.4622; d_4^{20} 1.0603; found MR 54.71; calculated MR 54.68.
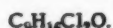
	Found %:	C 50.91; 51.04;	H 7.45; 7.50
$C_9H_{16}Cl_2O$.	Calculated %:	C 51.23;	H 7.58

1,1-Dichloro-9-ethoxy-1-nonene. This was prepared similarly to 1,1-dichloro-7-ethoxy-1-heptene in 73.5% yield. It had b.p. 88-89° (1 mm); n_D^{20} 1.4669; d_4^{20} 1.1054; found MR 63.81; calculated MR 64.00
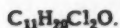
	Found %:	C 55.45; 55.41·,	H 8.21; 8.32
$C_{11}H_{20}Cl_2O$.	Calculated %:	C 55.23	H 8.36

5,5-Dichloro-N,N-diethyl-4-pentenylamine. A solution of 50 g of 1,1,5-trichloro-1-pentene and 50 g of diethylamine in 120 ml of methanol was heated in an autoclave at 100-115° for 5-6 hours. Excess of diethylamine and methanol was driven off from a water bath, and the residue was treated with hydrochloric acid. The undissolved oil was extracted with ether. The hydrochloric acid solution was rendered alkaline with cooling, and the oil that separated was extracted with ether. The product was 51.2 g (83.5%) of 5,5-dichloro-N,N-diethyl-4-pentenylamine, b.p. 63-64° (2 mm); n_D^{20} 1.4719; d_4^{20} 1.0349; found MR 56.81; calculated MR 56.93.
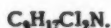
	Found %:	C 51.77; 51.55;	H 8.29; 8.16
$C_9H_{17}Cl_2N$.	Calculated %:	C 51.43;	H 8.09

7,7-Dichloro-N,N-diethyl-6-heptenylamine. This was prepared similarly to 5,5-dichloro-N,N-diethyl-4--pentenylamine in 88% yield. It had b.p. 89-90° (1.5 mm); n_D^{20} 1.4730; d_4^{20} 1.0097. Found MR 66.14; Calculated MR 66.21.

	Found %:	N 6.09; 6.18
$C_{11}H_{21}Cl_2N$.	Calculated %:	N 5.88

1,1-Dichloro-9-ethylthio-1-nonene. This was prepared by heating 1,1,9-trichloro-1-nonene with a small excess of C_2H_5SNa in alcoholic solution; the yield was 92.8%. It had b.p. 120-121° (1 mm); n_D^{20} 14991; d_4^{20} 1.0672. Found MR 70.17; Calculated MR 70.26.

	Found %:	C 51.62; 51.58;	H 7.70; 7.88
$C_{11}H_{20}Cl_2S$.	Calculated %:	C 51.76;	H 7.84

1,1-Dichloro-5-phenoxy-1-pentene. A solution of 1,1,5-trichloro-1-pentene (40 g), sodium iodide (1.5 g), and sodium phenoxide (from 28 g of phenol) in 100 ml of alcohol was heated for 8 hours 30 minutes. The product was 37. 6 g (70.5%) of 1,1-dichloro-5-phenoxy-1-pentene, b.p. 112-113° (2 mm); n_D^{20} 1.5375; d_4^{20} 1.1914.

TABLE 1

Formula of substance $R\text{-}C\equiv CH$	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Molecular refraction		Found		Calculated	
					found	calculated	C	H	C	H
$n\text{-}C_5H_{11}C\equiv CH$	68	97—98	1.4120	—	—	—	—	—	—	—
$n\text{-}C_6H_{13}C\equiv CH$	71	148—150	1.4250	—	—	—	—	—	—	—
$C_2H_5O(CH_2)_3C\equiv CH$	72	126—127	1.4204	0.8268	34.31	34.17	74.77; 74.92	10.56; 10.40	75.00	10.71
$C_3H_7O(CH_2)_3C\equiv CH$	76	63—64 (10)	1.4289	0.8318	43.38	43.24	77.28; 77.37	11.52; 11.70	77.15	11.43
$C_4H_9O(CH_2)_3C\equiv CH$	76	94—95 (10)	1.4350	0.8336	52.59	52.64	78.51; 78.44	12.06; 12.09	78.57	11.90
$C_4H_9O(CH_2)_3C\equiv CH$	87	108—109 (9)	1.5210	0.9848	49.47	49.07	82.18; 82.22	7.91; 7.81	82.37	7.50
$(C_2H_5)_2N(CH_2)_3C\equiv CH$ a	86	45—46 (8)	1.4410	0.8061	45.53	45.64	77.92; 77.70	12.14; 12.12	77.69	12.23
$(C_2H_5)_2N(CH_2)_3C\equiv CH$ b	78	84—85 (10)	1.4460	0.8128	54.79	54.58	—	—	—	—
$C_2H_5S(CH_2)_3C\equiv CH$	90	129—130 (12)	1.4771	0.8854	58.73	58.92	71.27; 71.37	10.73; 10.87	71.73	10.87
$(C_4H_9O)_2CH\text{-}C\equiv CH$	75	118—120 (27)	1.4280	0.8752	54.09	54.22	71.76; 71.54	10.83; 11.02	71.73	10.87
$n\text{-}C_3H_7CH\text{-}C\equiv CH$ (OC_2H_5)	40	45—46 (9)	1.4208	0.8229	43.12	43.24	77.28; 77.32	11.54; 11.60	77.15	11.43

a) Oxalate, m.p. 105;106° (from alcohol) Found %: N 6.23; 6.35; Calculated %: N 6.39

b) Found %: N 8.44; 8.55; Calculated %: N 8.38; oxalate, m.p. 72;73° (from alcohol-ether)

Found %: N 5.52; 5.48; Calculated %: N 5.44.

c) Found %: S 17.30; 17.40; Calculated %: S 17.38.
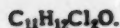
$C_{11}H_{12}Cl_2O.$ Calculated %: C 57.14; H 5.20

1,1,-Dichloro-3-ethoxy-1-heptene. An ethereal solution butylmagnesium bromide (from 30 g of butyl bromide and 5 g of magnesium was added gradually to a stirred ice-cooled solution of 37 g of 1,1,3-trichloro-3-ethoxypropene in 50 ml of dry ether. When the addition was complete, the mixture was stirred at room temperature for 30 minutes and poured into water (under cooling). The ether solution was washed with dilute hydrochloric acid and then with water; it was dried over potassium carbonate. Vacuum distillation yielded 31.2 g of 1,1-dichloro-3-ethoxy-1-heptene, b.p. 84-85° (9 mm); n_D^{20} 1.4530; d_4^{20} 1.0408; Found MR 54.79; Calculated MR 54.67.
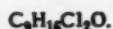
Found %: C 51.01; 50.95; H 7.52; 7.66
$C_9H_{16}Cl_2O.$ Calculated %: C 51.18; H 7.58

1,1-Dichloro-3,3-dibutoxypropene. This was prepared as already described [9].

Preparation of Acetylenes. A small amount of ethereal solution of the dichlorovinyl derivative was added to a stirred mixture of 0.38 g-atom of finely granulated sodium and 80-100 ml of dry ether, and the mixture was heated for a short time until reaction began. Heating was discontinued, and the remainder of the ethereal solution of the 2,2-dichlorovinyl derivative (0.1 mole) was added gradually, the rate of addition being regulated so that the ether was maintained at a vigorous boil. A precipitate of sodium derivative and sodium chloride formed gradually. The addition of the dichloro compound required 30-90 minutes, and when this was complete the reaction mixture was heated in a water bath to complete the reaction. It was then cooled with a freezing mixture and stirred while water was added cautiously. The ether layer was separated and dried. The monosubstituted acetylene formed was isolated by fractionation.

Action of Sodium on 1,1-Dichloro-9-ethylthio-1-nonene. When 22 g of 1,1-dichloro-9-ethylthio-1-nonene was treated with 7.5 g of sodium, 30 ml of hydrogen separated. When the reaction mixture was treated with water, 1100 ml of hydrogen was collected (theory requires 1050 ml). The ethereal solution was washed with water and dried with calcium chloride. Vacuum distillation yielded 14.2 g (90%) of 9-ethylthio-1-nonyne, b.p. 129-130° (12 mm); n_D^{20} 1.4771; d_4^{20} 0.8854.

4,5,5-Trichloro-N,N-diethyl-4-pentenylamine. A solution of 22 g of 1,1,2,5-tetrachloro-1-pentene and 20 g of diethylamine in 60 ml of methanol was heated in an autoclave at 100-110° for 5-6 hours. Excess of diethylamine and methanol was removed from a water bath, and the residue was treated with dilute hydrochloric acid. The undissolved oil was extracted with ether. The hydrochloric acid solution was rendered alkaline with cooling, and was then extracted with ether. Vacuum distillation yielded 19.8 g (76%) of 4,4,5-trichloro-N,N-diethyl-4-pentenylamine, b.p. 84-85° (2 mm); n_D^{20} 1.4886; d_4^{20} 1.1378; Found MR 61.98; Calculated MR 61.84.
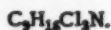
Found %: N 5.90; 5.89
$C_9H_{16}Cl_3N.$ Calculated %: N 5.73

Its oxalate melted at 125-126° (from alcohol-ether)
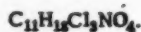
Found %: N 4.34; 4.34
$C_{11}H_{18}Cl_3NO_4.$ Calculated %: N 4.18

N,N-Diethyl-4-pentynylamine. A small amount of an ethereal solution of 4,5,5-trichloro-N,N-diethyl-4-pentenylamine was added to a mixture of 5.3 g of finely granulated sodium and 50 ml of ether. When the mixture had been heated, with stirring, for 15 minutes, reaction set in and the ether boiled without external application of heat. The remainder of the trichloro compound was then added dropwise. At first the reaction mixture acquired a dirty dark-blue color, but toward the end of the reaction it became white. The mixture was heated until the sodium disappeared, and it was then cooled and decomposed with water. The product was 7 g (88%) of N,N-diethyl-4-pentynylamine, b.p. 54° (10 mm); n_D^{20} 1.4412.

Action of Sodium on (3,3-Dichloroallyl)benzene. Treatment of 32 g of (3,3-dichloroallyl)benzene with 13 g of sodium by the usual method yielded 8 g of a product boiling at 60-65° (11 mm) and a large amount of nondistilling residue. Fractionation yielded a compound having b.p. 69-70° (11 mm), n_D^{20} 1.5800; d_4^{20} 0.9360; it appeared to be phenylpropadiene.

Found %: C 93.42; 93.23; H 6.93; 7.02
$C_9H_8.$ Calculated %: C 93.10; H 6.90

When hydrogenated, it absorbed two molecular proportions of hydrogen.

2-Hexynoic Acid. Solid carbon dioxide was added to the reaction mixture obtained by the action of 12 g of sodium on 20 g of 1,1-dichloro-1-pentene. After the mixture had been decomposed with water, the aqueous layer was acidified with hydrochloric acid, and the oil that separated was extracted with ether. Vacuum distillation yielded 5.2 g (32%) of 2-hexynoic acid, b.p. 116-117° (13 mm) and n_D^{20} 1.4642. The literature [10] gives b.p. 120° (16 mm), n_D^{20} 1.4650, and m.p. 27°.

6-Diethylamino-1-phenyl-2-hexyn-1-ol. A solution of 8 g of benzaldehyde in 10 ml of ether was added, with cooling and stirring, to the reaction mixture obtained by treating 11 g of 5,5-dichloro-N,N-diethyl-4-pentenylamine with 8.6g of sodium. The mixture was heated in a water bath for 30 minutes, cooled, and decomposed with water. The ethereal solution was extracted with dilute hydrochloride acid . The hydrochloric acid solution was rendered alkaline, and the oil that separated was extracted with ether. Distillation yielded 5.2 g of 6-diethylamino-1-phenyl-2-hexyn--1-ol, b.p. 172-173° (2 mm); n_D^{20} 1.5327; d_4^{20} 1.0006; Found MR 75.96; Calculated MR 75.97.
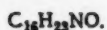
	Found %:	N 5.89; 5.99
$C_{16}H_{23}NO$.	Calculated%:	N 5.72

6-Ethoxy-1-phenyl-2-hexyn-1-ol. 5-Ethoxy-1-pentyne (9.5 g) was added gradually to an ethereal solution of ethylmagnesium bromide (prepared from 12.5 g of ethyl bromide and 2.8 g of magnesium). The solution was heated until ethane ceased to be evolved. Benzaldehyde (15 g) was then added gradually with cooling and stirring, after which the mixture was heated for one hour, cooled, and decomposed with saturated ammonium chloride solution. Vacuum distillation yielded 16.1 g (87%) of 6-ethoxy-1-phenyl-2-hexyn-1-ol, b.p. 185-186° (3 mm); n_D^{20} 1.5265; d_4^{20} 1.0284.
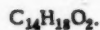
	Found %:	C 77.24; 77.22;	H 8.20; 8.23
$C_{14}H_{18}O_2$.	Calculated%:	C 77.08;	H 8.25

SUMMARY

1. The action of sodium on 2,2-dichlorovinyl derivatives was studied, and it was shown that monosubstituted acetylenes were formed in 60-80% yield in most of the cases investigated.

2. A mechanism is proposed for the conversion of a $CCl_2 = CH$ group into an $HC \equiv C$ group by the action of sodium.

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SYNTHESIS OF ALKYL BIS[1-(DIETHOXYPHOSPHINYL)ALKYL] PHOSPHITES

P. I. Alimov and I. V. Cheplanova

Triesters of phosphorous acid were first prepared in the middle of the last century, and since then many compounds of this class have been synthesized [1]. Study of mixed phosphorous triesters began comparatively recently (1930-1940); mixed esters reported include alkyl diaryl and dialkyl aryl phosphites [2], 2-chloroethyl diethyl and bis(2-chloroethyl) ethyl phosphites [3], and also cyclic esters   alkyl alkylene phosphites (glycol derivatives) and alkyl (aryl) arylene phosphites (pyrocatechol derivatives) [4]. •

This paper describes the syntheses of organophosphorus compounds containing three phosphorus atoms, their general formula being

$$ROP \diagup \begin{matrix} O-C(R_1R_2)-P(OC_2H_5)_2 \\ \parallel \\ O \\ \\ O-C(R_1R_2)-P(OC_2H_5)_2 \\ \parallel \\ O \end{matrix}$$
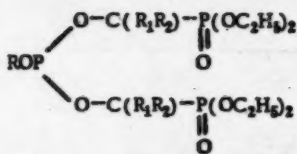
(R and R_1 are alkyl groups, and R_2 is H or alkyl).

These compounds can be regarded as mixed phosphorous esters — alkyl bis[1-(diethoxyphosphinyl)alkyl] phosphites— in which one ester grouping contains an aliphatic alcohol residue and the other two contain residues of a diethyl 1-hydroxyalkylphosphonate.

The substances were synthesized by reaction of alkyl phosphorodichloridites with diethyl 1-hydroxyalkylphosphonates in presence of tertiary amines for the binding of hydrogen chloride, for example:

$$C_2H_5OPCl_2 + 2HO-\underset{\underset{CH_3}{|}}{C}H-\underset{\underset{O}{\parallel}}{P}(OC_2H_5)_2 + 2(C_2H_5)_3N \longrightarrow$$

$$\longrightarrow C_2H_5OP \diagup \begin{matrix} O-CH-P(OC_2H_5)_2 \\ | \quad \parallel \\ CH_3 \ O \\ \\ O-CH-P(OC_2H_5)_2 \\ | \quad \parallel \\ CH_3 \ O \end{matrix} \qquad + 2(C_2H_5)_3N \cdot HCl$$
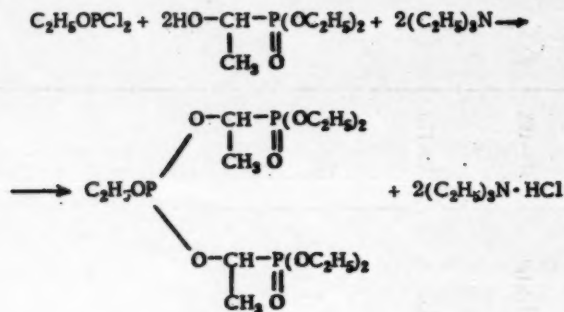
The reaction was carried out in an organic solvent — ether or gasoline— at first at room temperature, and then at 50-60°. The reactants used were the diethyl esters of 1-hydroxyethyl-, 1-hydroxy-1-methylethyl-, and 1-hydroxy--1-methylpropyl-phosphonic acids, which were prepared by Abramov's method [5], and the methyl, ethyl, and propyl esters of phosphorodichloridous acid. The table gives the formulas, physical constants, and yields of the products.

The substances listed in the table are colorless mobile liquids having a feeble ethereal odor; they are soluble in water and in organic solvents. The experimentally determined molecular refractions of these compounds are lower— by one unit, on the average— than the calculated values. These discrepancies are probably to be attributed to changes in the atomic refraction of phosphorus arising from peculiarities in the structures of the compounds. In the molecular refraction calculations we took the atomic refraction of phosphorus to be 7.04 for the tervalent state and 4.27 for phosphorus in the alkylphosphonic residue [6].

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* This statement is obsure, but is clarified by reference to abstracts of original papers — Publishers

TABLE

No.	Formula	B.p. (°C)	Pressure (mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated	Yield (%)
1	$C_2H_5OP[O-CH-P(OC_2H_5)_2]_2$ CH_3 O	162—164	(0.1)	1.4479	1.1579	101.3	101.7	38.9
2	$n\text{-}C_3H_7OP[O-CH-P(OC_2H_5)_2]_2$ CH_3 O	167—168	(0.035)	1.4477	1.1476	105.3	105.3	33.8
3	$CH_3OP[O-C(CH_3)_2-P(OC_2H_5)_2]_2$ O	172—173	(1)	1.4505	1.1592	104.9	103.32	28.7
4	$C_2H_5OP[O-C(CH_3)_2-P(OC_2H_5)_2]_2$ O	172—173	(0.5)	1.4500	1.1370	110.1	110.9	34
5	$C_2H_5OP\left[O-C\begin{smallmatrix}CH_3\\ \\ \end{smallmatrix}-P(OC_2H_5)_2\right]_2$ $C_2H_5 \, O$	181—183	(1)	1.4562	1.1303	118.8	120.18	9.9
6	$n\text{-}C_3H_7OP[O-C(CH_3)_2-P-(OC_2H_5)_2]_2$ O	175—176	(0.35)	1.4494	1.1243	114.6	115.6	50.1

Alkyl bis[1-(diethoxyphosphinyl)alkyl] phosphites are hydrolyzed by dilute hydrochloric acid at the boil with formation of phosphorous acid and 1-hydroxyalkylphosphonic acids. Phosphorous acid, so formed, was determined quantitatively by a method based on its ability to reduce mercuric chloride to mercurous chloride [7].

Being tervalent phosphorus derivatives, alkyl bis[1-(diethylphosphinyl)alkyl] phosphites readily unite with cuprous halides [8] and with sulfur [9]. The latter reaction yields O-alkyl O,O-bis[1-(diethoxyphosphinyl)alkyl] phosphorothioates, for example:

$$
\begin{array}{c}
OCH-P(OC_2H_5)_2 \\
\mid \quad \parallel \\
CH_3 \ O \\
C_2H_5OP \\
\parallel \\
S \\
O-CH-P(OC_2H_5)_2 \\
\mid \quad \parallel \\
CH_3 \ O
\end{array}
$$
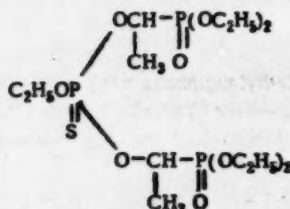
EXPERIMENTAL

I. Synthesis of Alkyl Bis[1-(diethoxyphosphinyl) alkyl] Phosphites

1. Ethyl Bis[1-(diethoxyphosphinyl)ethyl] Phosphite

$$C_2H_5OP[O-CH-P OC_2H_5)_2]$$
$$\mid \quad \parallel$$
$$CH_3 \ O$$
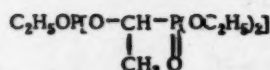
A mixture of 26 g of diethyl 1-hydroxyethylphosphonate [5] (b.p. 130-131°/6 mm), 14.4 g of methylamine, and 140 ml of gasoline (b.p. 75-125°) was prepared in a three-necked, round-bottomed flask fitted with mechanical stirrer, dropping funnel, and reflux condenser. Ethyl phosphorodichloridite (10.5 g) was added gradually from the dropping funnel at room temperature. Triethylamine hydrochloride then separated. When addition of the dichloridite was complete, the reaction mixture was stirred for two hours at a bath temperature of 50-60°. When the mixture was cool, triethylamine hydrochloride was filtered off and washed with ether. After removal of solvent a residue (30.2 g, i.e. 96.4%) of light-yellow mobile liquid remained. Distillation from an Arbuzov flask gave the following fractions:

Fraction I	b.p. 115-160° (0.1 - 0.075 mm);	6.5 g
Fraction II	b.p. 160-165° (0.075 mm);	13.9 g
Residue		7.3 g

Redistillation of Fraction II yielded 12.2 g of a substance having the following constants: b.p. 162-164° (0.1 mm); n_D^{20} 1.4479, d_4^{20} 1.1579; The yield was 38.9%.
Found MR 101.3. Calculated $C_{14}H_{23}P_3O_9$ MR 101.7.

	Found %:	P 21.18; 21.35
$C_{14}H_{33}P_3O_9$.	Calculated%:	P 21.23

This substance was a colorless, almost odorless, highly mobile liquid, readily soluble in water, ether, alcohol, and other organic solvents.

2. Propyl Bis[1-(diethoxyphosphinyl)ethyl]Phosphite

$$n-C_3H_7OP[O-CH-P(OC_2H_5)_2]_2$$
$$\mid \quad \parallel$$
$$CH_3 \ O$$
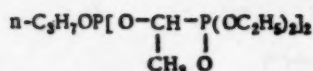
The reactants were diethyl 1-hydroxyethylphosphonate (21 g), triethylamine (11.7 g), and propyl phosphorodichloridite (9.3 g). The reaction conditions were as in the first experiment. After removal of triethylamine hydrochloride and solvent, there was a residue, amounting to 27.8 g (99.2%), of a light-yellow mobile liquid. Distillation yielded the fractions.

Fraction I	b.p. 110-167° (0.05-0.035 mm);	10.5 g
Fraction II	b.p. 167-168° (0.035 mm);	8.8 g
Fraction III	b.p. 168-174° (0.035 mm);	2.9 g
Residue		2.1 g

The yield of Fraction II was 33.7%; it had MR 106.3. n_D^{20} 1.4477; d_4^{20} 1.1476; Found MR 105.3; Calculated $C_{15}H_{36}P_3O_9$

$C_{15}H_{36}P_3O_9$.
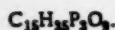
Found %: P 20.90; 20.92
Calculated %: P 20.57

3. Methyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite

$$CH_3OP \, [O-C(CH_3)_2-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2]_2$$
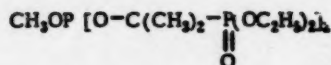
Reaction of 25 g of diethyl 1-hydroxy-1-methylethylphosphonate [5] (b.p. 130-131°, 10 mm), 8.5 g of methyl phosphorodichloridite, and 13 g of triethylamine in gasoline (130 ml; b.p. 75-125°) solution yielded 29 g of crude product after removal of triethylamine hydrochloride and solvent. Distillation yielded the fractions:

        Fraction I   b.p.   105 - 155° (1 mm);   3.8 g
        Fraction II   b.p.   155 - 176° (1 mm);   19.8 g
        Residue   4 g

Redistillation of Fraction II gave:

        Fraction I   b.p.   60 - 172° (1 mm);   8.9 g
        Fraction II   b.p.   172 - 173° (1 mm);   7.7 g
        Residue   2 g

The yield of Fraction II, b.p. 172-173° (1 mm), was 26.7%. It had n_D^{20} 1.4505; d_4^{20} 1.1592; Found MR 104.9; Calculated $C_{15}H_{35}P_3O_9$ MR 106.32.
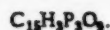
Found %: P 20.93; 20.86
$C_{15}H_3P_3O_9$.   Calculated %: P 20.57

The substance was a colorless, highly mobile liquid having a feeble odor. It was readily soluble in water and in organic solvents.

4. Ethyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite

$$C_2H_5OP[O-C(CH_3)_2-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2]_2$$
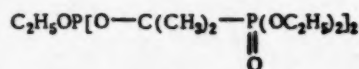
Reaction was between 25 g of diethyl 1-hydroxy-1-methylethylphosphonate, 12.9 g of triethylamine, and 9.4 g of ethyl phosphorodichloridite. The weight of crude product was 27.1 g (91.2%). Distillation yielded the fractions:

        Fraction I   b.p.   105 - 158° (0.5 mm);   5.5 g
        Fraction II   b.p.   158 - 176° (0.5 mm);   16.6 g
        Residue   3 g

Distillation of Fraction II yielded 10.1 g (34%) of a substance having b.p. 172-173° (0.5 mm); n_D^{20} 1.4500; d_4^{20} 1.1370 Found MR 110.1; Calculated $C_{16}H_{37}P_3O_9$ MR 110.9
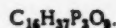
Found %: P 20.19; 20.27
$C_{16}H_{37}P_3O_9$.   Calculated %: P 19.95

This substance was a colorless mobile liquid of feeble odor.

5. Ethyl Bis[1-(diethoxyphosphinyl)-1-methylpropyl] Phosphite

$$C_2H_5OP[O-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{P}(OC_2H_5)_2]_2$$
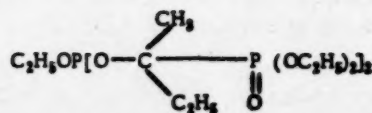
Reaction was between 25.8 g of diethyl 1-hydroxy-1-methylpropylphosphonate (b.p. 135-136°, 11 mm), 12.4 g of triethylamine, and 9 g of ethyl phosphorodichloridite.   The yield of crude product was 28.8 g (95%).   Distillation gave:

Fraction I   b.p.   100-170° (0.1 - 0.04 mm);   14.9 g
Fraction II b.p.   170-174° (0.04 mm);   10 g

Redistillation of Fraction II gave 3 g (9.9%) of a substance having b.p. 181-183° (1 mm); n_D^{20} 1.4562; d_4^{20} 1.1303; Found MR 118.3; Calculated $C_{16}H_{41}P_3O_9$ MR 120.18.

$$C_{16}H_{41}P_3O_9.$$ Found %: P 19.08; 19.14
                          Calculated %: P 18.82

6. Propyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite

$$C_3H_7OP[O-C(CH_3)_2-P(OC_2H_5)_2]_2.$$
$$\qquad\qquad\qquad\qquad\quad \overset{\parallel}{O}$$
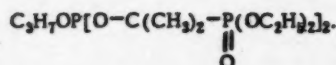
After reaction between 24.3 g of diethyl 1-hydroxy-1-methylethylphosphonate, 12.5 g of triethylamine, and 10 g of propyl phosphorodichloridite and removal of triethylamine hydrochloride and solvent, 28.3 g (95.2%) of crude product was obtained. Distillation yielded the fractions:

Fraction I   b.p.   90-175° (0.35 mm);   10.2 g
Fraction II b.p.   175-176° (0.35 mm); 14.9 g

The yield of Fraction II was 50.1%, and it had n_D^{20} 1.4494; d_4^{20} 1.1243; Found MR 114.6; Calculated $C_{17}H_{39}P_3O_9$ MR 115.6.

$$C_{17}H_{39}P_3O_9.$$ Found %: P 19.65; 19.67
                          Calculated %: P 19.38

It was a colorless mobile liquid, sparingly soluble in water, but readily soluble in organic solvents.

II. Reactions of Alkyl Bis[1-(diethoxyphosphinyl)alkyl] Phosphites

1. Hydrolysis of Propyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite.   A solution of 0.5833 g of the mixed ester (b.p. 175-176°, 0.35 mm) in 15 ml of 10% hydrochloric acid was boiled for 6 hours 30 minutes. An aqueous solution of 1.5 g (125% excess) of mercuric chloride was added to the hydrolysis products, and the mixture was then stirred at the boiling point for some time. Calomel, amounting to 0.5696 g (99.28%), was obtained.

2. Addition of Cuprous Iodide to Ethyl Bis[1-(diethoxyphosphinyl)-1-methylethyl] Phosphite.   Cuprous iodide (0.408 g) was added to 1 g (an equimolecular proportion) of the mixed ester (b.p. 172-173°, 0.5 mm). The mixture was heated to 145-150°, and almost the whole of the salt went into solution. The product was a thick clear liquid which did not crystallize after prolonged standing.

3. Addition of Sulfur to Ethyl Bis[1-(diethoxyphosphinyl)ethyl] Phosphite.   Sulfur powder (0.1333 g) was added to 1.8247 g of the mixed ester (b.p. 162-164°, 0.1 mm; n_D^{20} 1.4595; d_4^{20} 1.1937; Found MR 107.7; Calculated $C_{14}H_{33}P_3O_9S$ MR 108.075.

$$C_{14}H_{33}P_3O_9S.$$ Found %: P 19.95; 19.82
                           Calculated %: P 19.70

The product was a thick, colorless, almost odorless liquid. It was soluble in organic solvents, but only sparingly soluble in water.

SUMMARY

1. The synthesis is described of mixed phosphorous esters in which diethoxyphosphinyl groups are present as substituents in the hydrocarbon radicals, i.e. alkyl bis[1-(diethoxyphosphinyl)alkyl] phosphites;

ROP
$$O-C(R_1R_2)-P(OC_2H_5)_2$$
$$\parallel$$
$$O$$
$$O-C(R_1R_2)-P(OC_2H_5)_2$$
$$\parallel$$
$$O$$
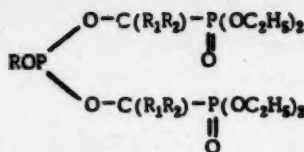
(R is CH_3, C_2H_5 or $n-C_3H_7$; R_1 is H or CH_3; and R_2 is CH_3 or C_2H_5).

2. Some of the properties of these mixed esters are described.

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ESTERS OF ETHYLPHOSPHONOUS ACID, AND SOME OF THEIR REACTIONS

COMMUNICATION 6. TRIETHYLPHOSPHONAMIDOUS ESTERS

B. A. Arbuzov, N. I. Rizpolozhensky, and M. A. Zvereva

In continuation of our work on the properties of ethylphosphonous esters, we have synthesized triethylphosphonamidous esters and studied some of their properties. The results of this work are described in the present paper. These esters have not been described previously in the literature.

The triethylphosphonamidous esters were synthesized from triethylphosphonamidous chloride, which was itself prepared by the action of diethylamine on ethylphosphonous dichloride in a medium of absolute ether:

$$C_2H_5PCl_2 + 2(C_2H_5)_2NH \rightarrow C_2H_5P \begin{array}{l} N(C_2H_5)_2 \\ \\ Cl \end{array} + (C_2H_5)_2NH \cdot HCl.$$
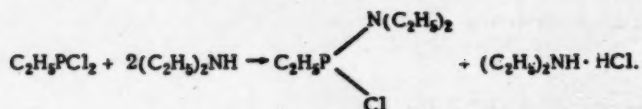
The yield of the acid chloride was about 80%. Triethylphosphonamidous chloride is colorless mobile liquid which fumes strongly in the air. It is very rapidly decomposed by atmospheric moisture with the separation of diethylamine hydrochloride. The acid chloride has a very unpleasant, penetrating odor.

When triethylphosphonamidous chloride is treated with ethanol in a medium of absolute ether, diethyl ethylphosphonite and diethylamine hydrochloride are formed. This reaction can be expressed by the equation:

$$C_2H_5P \begin{array}{l} N(C_2H_5)_2 \\ \\ Cl \end{array} + 2C_2H_5OH \rightarrow C_2H_5P(OC_2H_5)_2 + (C_2H_5)_2NH \cdot HCl$$
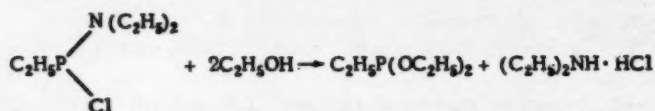
Triethylphosphonamidous esters were prepared by the action of alcohols on triethylphosphonamidous chloride in a medium of absolute ether in presence of triethylamine:

$$C_2H_5P \begin{array}{l} N(C_2H_5)_2 \\ \\ Cl \end{array} + ROH + (C_2H_5)_2N \rightarrow C_2H_5P \begin{array}{l} N(C_2H_5) \\ \\ OR \end{array} + (C_2H_5)_2N \cdot HCl$$
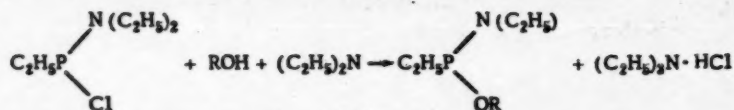
In this way triethylphosphonamidous esters, ranging from the methyl to the decyl ester, were prepared in yields ranging from 77% down to 22% (Table 1). Triethylphosphonamidous esters are colorless mobile liquids having an unpleasant phosphine odor. They readily combine with sulfur with formation of O-esters of triethylphosphonamidothioic acid:

$$C_2H_5P \begin{array}{l} N(C_2H_5)_2 \\ \\ OR \end{array} + S \rightarrow C_2H_5P \begin{array}{l} N(C_2H_5)_2 \\ \| \\ OR \end{array}$$
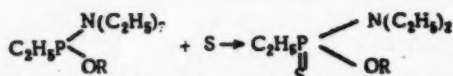
In this way previously undescribed O-esters of triethylphosphonamidothioic acid — ranging from the methyl to the decyl ester — were prepared. The principal constants of these esters are given in Table 2. O-Alkyl triethylphosphonamidothioates are colorless mobile liquids of unpleasant odor. They are insoluble in water, but readily soluble in alcohol, ether, gasoline, and benzene.

TABLE 1

No.	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Found MR	Calculated MR	Yield (%)
1	C_2H_5P < Cl / $N(C_2H_5)_2$	52—53 (3)	~0.9964	~1.4836	—	—	77
2	C_2H_5P < OCH_3 / $N(C_2H_5)_2$	49—50 (10)	0.8954	1.4450	48.44	48.20	72
3	C_2H_5P < OC_2H_5 / $N(C_2H_5)_2$	53—54 (9)	0.8847	1.4418	53.80	52.82	63
4	C_2H_5P < OC_3H_7-n / $N(C_2H_5)_2$	73—74 (10)	0.8820	1.4439	57.70	57.44	65
5	C_2H_5P < OC_3H_7-iso / $N(C_2H_5)_2$	63—65 (10)	0.8730	1.4400	57.59	57.44	61
6	C_2H_5P < OC_4H_9-n / $N(C_2H_5)_2$	88—89 (10)	0.8800	1.4450	62.09	62.15	61.7
7	C_2H_5P < OC_4H_9-iso / $N(C_2H_5)_2$	79—80 (10)	0.8739	1.4423	62.19	62.15	71
8	C_2H_5P < OC_6H_{13} / $N(C_2H_5)_2$	80—81 (1)	0.8787	1.4500	71.37	71.29	6
9	C_2H_5P < OC_7H_{15} / $N(C_2H_5)_2$	101—102 (1)	0.8794	1.4513	75.73	75.21	40
10	C_2H_5P < OC_8H_{17} / $N(C_2H_5)_2$	115—116 (2)	0.8794	1.4528	80.31	80.53	30
11	$C_{21}H_5P$ < OC_9H_{19} / $N(C_2H_5)_2$	121—122 (2)	0.8800	1.4550	84.93	85.15	27
12	C_2H_5P < $OC_{10}H_{21}$ / $N(C_2H_5)_2$	134—135 (2)	0.8806	1.4569	89.50	89.76	22

EXPERIMENTAL

I. Synthesis of Triethylphosphonamidous Esters

1. Triethylphosphonamidous Chloride. A mixture of 85 g of ethylphosphonous dichloride and 500 ml of absolute ether was prepared in a 750-ml four-necked flask fitted with mercury-sealed mechanical stirrer, reflux condenser, tube for the passage of carbon dioxide, and dropping funnel. The flask was cooled with ice and salt, carbon dioxide was passed through slowly, and 95 g of diethylamine was added over a period of two hours from the dropping funnel. The cooling mixture was then removed, and the reaction products were stirred at room temperature for about three hours. Diethylamine hydrochloride was filtered off at the pump and washed several times on the filter with absolute ether.

Ether was distilled from the filtrate, and the residue was vacuum-fractionated, when triethylphosphonamidous chloride, b.p. 52-53° (3 mm), was isolated. It was obtained as a colorless mobile liquid having an unpleasant penetrating odor. It reacted with water with bursts of flame. The acid chloride decomposed very rapidly in the air with the separation of crystalline products (diethylamine hydrochloride). The density and refractive index of the acid chloride were measured in an atmosphere of dry carbon dioxide, but in spite of this precaution, decomposition of the acid chloride was observed in the pycnometer and more particularly, in the refractometer (precipitation of crystals). Our values for these constants are therefore not altogether accurate: $d_4^{20} \approx 0.9964$; $n_D^{20} \approx 1.4836$.
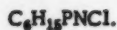
	Found %:	P 18.2; 18.25
$C_6H_{15}PNCl$.	Calculated %:	P 18.55

The yield of triethylphosphonamidous chloride was 83 g (77%).

2. Methyl Triethylphosphonamidite. The ester was synthesized in the apparatus described in detail above. A mixture of 2 g of methanol, 15 g of triethylamine, and 150 ml of absolute ether was prepared in the reaction flask. Triethylphosphonamidous chloride (21.5 g) was added from the dropping funnel over a period of one hour, the reaction flask being cooled with a freezing mixture. The cooling mixture was then removed, and the reaction products were stirred at room temperature for 2.5-3 hours. The precipitate of triethylamine hydrochloride was filtered off at the pump and washed three or four times with absolute ether.

Ether was distilled from the filtrate, and the residue was vacuum-fractionated from an Arbuzov flask. The methyl triethylphosphonamidite then obtained had b.p. 49-50° (10 mm); d_4^{20} 0.8954; n_D^{20} 1.4450.
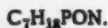
	Found MR	48.44
$C_7H_{18}PON$.	Calculated MR	48.20
	Found %:	P 19.2; 19.25
$C_7H_{18}PON$.	Calculated %:	P 19.00

The yield of ester was 15.2 g (72%). Methyl triethylphosphonamidite is a colorless mobile liquid having a very unpleasant odor.

3. Ethyl Triethylphosphonamidite. In the preparation of this ester, and of all the remaining esters, the apparatus and procedure were essentially the same as for methyl triethylphosphonamidite. The reactants taken for the synthesis of the ethyl ester were 5.6 g of ethanol, 13.5 g (1.5 g excess) of triethylamine, and 20 g of triethylphosphonamidous chloride in 150 ml of absolute ether. Ethyl triethylphosphonamidite has b.p. 53-54° (9 mm); d_4^{20} 0.8847, n_D^{20} 1.4418.
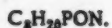
	Found MR	53.80
$C_8H_{20}PON$.	Calculated MR	52.82
	Found %:	P 17.65; 17.68
$C_8H_{20}PON$.	Calculated %:	P 17.5
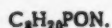
The ester has a very unpleasant odor. The yield was 13.3 g (63%).

4. Propyl Triethylphosphonamidite. The ester was prepared from 8.55 g of propyl alcohol, 16 g (1.6 g excess) of triethylamine, and 23.8 g of triethylphosphonamidous chloride in 150 ml of absolute ether. Vacuum fractionation yielded propyl triethylphosphonamidite having b.p. 73-74° (10 mm); d_4^{20} 0.8820; n_D^{20} 1.4439.
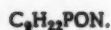
	Found MR	57.70
$C_9H_{22}PON$.	Calculated MR	57.44

The ester has an unpleasant odor. The yield was 17.2 g (65%).

5. Isopropyl Triethylphosphonamidite. The ester was prepared in 120 ml of absolute ether from 5.9 g of isopropyl alcohol, 11 g of triethylamine, and 16.1 g of triethylphosphonamidous chloride; its constants were b.p. 63-65° (9 mm); d_4^{20} 0.8730; n_D^{20} 1.4400.

TABLE 2

No.	Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	Found MR	Calculated MR*	Yield (%)
1	C_2H_5P $<$ Cl / $N(C_2H_5)_2$ ‖ S	94—95 (1)	1.1135	1.5205	54.55	54.68	80
2	C_2H_5P $<$ OCH_3 / $N(C_2H_5)_2$ ‖ S	112—113 (10)	1.0287	1.4882	54.63	54.84	69
3	C_2H_5P $<$ OC_2H_5 / $N(C_2H_5)_2$ ‖ S	115—116 (9)	1.0042	1.4828	59.48	59.55	73
4	C_2H_5P $<$ OC_3H_7-n / $N(C_2H_5)_2$ ‖ S	84—85 (1)	0.9892	1.4801	64.13	64.17	65
5	C_2H_5P $<$ OC_3H_7-i / $N(C_2H_5)_2$ ‖ S	118.5—119 (9)	0.9858	1.4781	64.13	64.17	67,5
6	C_2H_5P $<$ OC_4H_9-n / $N(C_2H_5)_2$ ‖ S	88—89 (1)	0.9789	1.4785	68.67	68.79	61,1
7	C_2H_5P $<$ OC_4H_9-ISO / $N(C_2H_5)_{12}$ ‖ S	132—133 (13)	0.9739	1.4750	68.60	68.79	63
8	C_2H_5P $<$ OC_6H_{13} / $N(C_2H_5)_2$ ‖ S	132—133 (1.5)	0.9642	1.4790	78.64	78.73	49.5
9	C_2H_5P $<$ OC_7H_{15} / $N(C_2H_5)_2$ ‖ S	137—137.5 (2)	0.9578	1.4789	82.74	82.65	32
10	C_2H_5P $<$ OC_8H_{17} / $N(C_2H_5)_2$ ‖ S	144—144.5 (1)	0.9516	1.4793	87.45	87.27	33.4
11	C_2H_5P $<$ OC_9H_{19} / $N(C_2H_5)_2$ ‖ S	151—152 (1)	0.9495	1.4796	91.91	91.88	25.6
12	C_2H_5P $<$ $OC_{10}H_{21}$ / $N(C_2H_5)_2$ ‖ S	170—172 (2.5)	0.9446	1.4800	96.67	96.51	19.2

* The atomic refraction of nitrogen was taken to be 2.09; the atomic refraction of phosphorus calculated from the results of the present work is 4.78 [1].

C$_9$H$_{22}$OPN.   Calculated MR 57.44

Found%: P 16.35; 16.21

C$_9$H$_{22}$OPN.   Calculated%: P 16.1

The yield of ester was 11.3 g (61%).

6. Butyl Triethylphosphonamidite. The substances taken for reaction were 6 g of butyl alcohol, 9.5 g of triethyl-amine, 120 ml of absolute ether, and 15.5 g of triethylphosphonamidous chloride. The constants of butyl triethylphosphonamidite are b.p. 88-89° (10 mm); d_4^{20} 0.8800; n_D^{20} 1.4450.

Found MR 62.09

C$_{10}$H$_{24}$OPN.   Calculated MR 62.15

Found%: P 15.26; 15.15

C$_{10}$H$_{24}$OPN.   Calculated%: P 15.1

The yield of ester was 11.7 g (61.7%).

7. Isobutyl Triethylphosphonamidite. This was prepared from 7.3 g of isobutyl alcohol, 12 g of triethylamine (2 g excess), and 16.6 g of triethylphosphonamidous chloride in 130 ml of absolute ether. The constants of the ester are b.p. 79-80° (10 mm); d_4^{20} 0.8739; n_D^{20} 1.4423.

Found MR 62.19

C$_{10}$H$_{24}$OPN.   Calculated MR 62.15

Found%: P 15.15; 15.17

C$_{10}$H$_{24}$OPN.   Calculated%: P 15.1

The yield of ester was 13.5 g (71%).

8. Hexyl Triethylphosphonamidite. This was prepared from 8 g of hexyl alcohol, 9 g of triethylamine, and 13.1 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The hexyl triethylphosphamidite so obtained had b.p. 80-81° (1 mm); d_4^{20} 0.8787; n_D^{20} 1.4500.

Found MR 71.37

C$_{12}$H$_{28}$PON.   Calculated MR 71.29

Found%: P 13.61; 13.50

C$_{12}$H$_{28}$PON.   Calculated%: P 13.32

The yield of ester was 11.1 g (61%).

9. Heptyl Triethylphosphonamidite. This ester was prepared from 9 g of heptyl alcohol, 8.5 g of triethylamine, and 12.8 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The heptyl triethylphosphonamidite so ob-tained had b.p. 101-102° (1 mm); d_4^{20} 0.879-; n_D^{20} 1.4513.

Found MR 75.73

C$_{13}$H$_{30}$PON.   Calculated MR 75.21

Found%: P 12.31; 12.38

C$_{13}$H$_{30}$PON.   Calculated%: P 12.58

The yield of ester was 7.6 g (40%).

10. Octyl Triethylphosphonamidite. This ester was prepared from 10.3 g of octyl alcohol, 9.5 g of triethylamine, and 13.2 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The ester obtained had b.p. 115-116° (2 mm); d_4^{20} 0.8794; n_D^{20} 1.4528.

Found MR 80.31

C$_{14}$H$_{32}$PON.   Calculated MR 80.53

Found%: P 12.22; 12.18

C$_{14}$H$_{32}$PON.   Calculated%: P 11.9

The yield of ester was 3.2 g (30%).

11. **Nonyl Triethylphosphonamidite.** The nonyl ester was prepared from 10.8 g of nonyl alcohol, 8.5 g of tri-ethylamine, and 16 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The ester obtained had the following constants: b.p. 121-122° (2 mm); d_4^{20} 0.8800; n_D^{20} 1.4550.

	Found MR 84.93		
$C_{15}H_{34}PON.$	Calculated MR 85.15		
	Found %: P 11.50;	11.51	
$C_{15}H_{34}PON.$	Calculated %: P 11.30		

The yield of ester was 7.1 g (27%).

12. **Decyl Triethylphosphonamidite.** The decyl ester was prepared from 12.5 g of decyl alcohol, 9 g of triethyl-amine, and 13.2 g of triethylphosphonamidous chloride in 100 ml of absolute ether. The decyl triethylphosphonamidite so obtained had the following constants: b.p. 134-135° (2 mm); d_4^{20} 0.9806; n_D^{20} 1.4569.

	Found MR 89.50
$C_{16}H_{36}PON.$	Calculated MR 89.76

The yield of ester was 5.4 g (22%).

II. Synthesis of O-Alkyl Triethylphosphonamidothioates

1. **Triethylphosphonamidothioic Chloride.** Triethylphosphonamidous chloride (9.2 g) was placed in a three-necked flask fitted with reflux condenser, thermometer, and tube for the passage of carbon dioxide. Sulfur powder (1.75 g) was added in portions to the acid chloride. The reaction did not go in the cold, and when the mixture was heated to 120° some of the sulfur dissolved, but it was reprecipitated on cooling. A few crystals of aluminum chloride were then added, and reaction began immediately. The temperature in the flask begain to rise rapidly, attaining 170° toward the end of the reaction, and the contents became brown. Vacuum distillation of the reaction products from an Arbuzov flask yielded triethylphosphonamidothioic chloride, b.p. 94-95°(1 mm); n_D^{20} 1.1135; d_4^{20} 1.5205.

	Found MR 54.55	
$C_6H_{15}PNSCl.$	Calculated MR 54.68	
	Found %: P 15.82;	15.6
$C_6H_{15}PNCl.$	Calculated %: P 15.55	

The yield of acid chloride was 8.8 g (80%).

2. **O-Methyl Triethylphosphonamidothioate.** Methyl triethylphosphonamidite (4.5 g) was placed in a three-necked flask fitted with thermometer, tube for the passage of carbon dioxide, and reflux condenser. Addition of sulfur to the ester was found to proceed very vigorously, and the sulfur was therefore added in small portions. The final portions of sulfur reacted sluggishly, but at 140-150° the whole (0.89 g) of the sulfur taken for reaction dissolved. Vacuum dis-tillation of the reaction product yielded O-methyl triethylphosphonamidothioate, b.p. 112-113° (10 mm); d_4^{20} 1.0287; n_D^{20} 1.4882.

	Found MR 54.63	
$C_7H_{18}PONS.$	Calculated MR 54.84	
	Found %: P 15.82; 15.9; S 16.21;	16.15
$C_7H_{18}PONS.$	Calculated %: P 15.79 S 16.05	

The yield of ester was 3.7 g (69%).

3. **O-Ethyl Triethylphosphonamidothioate.** The above-described procedure was followed. The reactants were ethyl triethylphosphonamidite (4.1 g) and sulfur (0.75 g). Vacuum fractionation of the reaction products from an Arbuzov flask yielded O-ethyl triethylphosphonamidothioate, b.p. 115-116° (9 mm); d_4^{20} 1.0042; n_D^{20} 1.4828.

	Found MR 59.48
$C_8H_{20}PONS.$	Calculated MR 59.55
	Found %: P 15.0; 14.95
$C_8H_{20}PONS.$	Calculated %: P 14.82

The yield of ester was 3.6 g (73%).

4. O-Propyl Triethylphosphonamidothioate.   The reactants were propyl triethylphosphonamidite (5 g) and sulfur (0.8 g). Vacuum distillation of the reaction product from an Arbuzov flask gave O-propyl triethylphosphonamidothioate, b.p. 84-85° (1 mm); d_4^{20} 0.9892; n_D^{20} 1.4801.

$$
\begin{array}{ll}
 & \text{Found MR 64.13} \\
\text{C}_9\text{H}_{32}\text{PONS.} & \text{Calculated MR 64.17} \\
 & \text{Found \%: P 14.11; 14.18} \\
\text{C}_9\text{H}_{32}\text{PONS.} & \text{Calculated \%: P 13.9}
\end{array}
$$

The yield of ester was 3.8 g (65%).

5. O-Isopropyl Triethylphosphonamidothioate. The reactant. were isopropyl triethylphosphonamidite (4.7 g) and flowers of sulfur (0.78 g). Vacuum fractionation of the reaction product from an Arbuzov flask gave O-isopropyl triethylphosphonamidothioate, b.p. 118.5-119° (9 mm); d_4^{20} 0.9858; n_D^{20} 1.4781.

$$
\begin{array}{ll}
 & \text{Found MR 64.13} \\
\text{C}_9\text{H}_{22}\text{PONS.} & \text{Calculated MR 64.17} \\
 & \text{Found \%: P 14.05; 14.12} \\
\text{C}_9\text{H}_{22}\text{PONS.} & \text{Calculated \%: P 13.9}
\end{array}
$$

The yield of ester was 3.7 g (67.5%).

6. O-Butyl Triethylphosphonamidothioate.   The ester was prepared from 6.2 g of butyl triethylphosphonamidite and 0.97 g of flowers of sulfur. Vacuum fractionation from an Arbuzov flask gave O-butyl triethylphosphonamidothioate, b.p. 88-89° (1 mm) ; d_4^{20} 0.9739; n_D^{20} 1.4750.

$$
\begin{array}{ll}
 & \text{Found MR 68.67} \\
\text{C}_{10}\text{H}_{24}\text{PONS.} & \text{Calculated MR 69.79} \\
 & \text{Found \%: P 13.28; 13.11} \\
\text{C}_{10}\text{H}_{24}\text{PONS.} & \text{Calculated \%: P 13.18}
\end{array}
$$

The yield of ester was 4.4 g (61%).

7. O-Isobutyl Triethylphosphonamidothioate. The ester was prepared from 4 g of isobutyl triethylphosphonamidite and 0.62 g of flowers of sulfur. Vacuum distillation from an Arbuzov flask gave O-isobutyl triethylphosphonamidothioate, b.p. 132-133° (13 mm); d_4^{20} 0.9739; n_D^{20} 1.4750.

$$
\begin{array}{ll}
 & \text{Found MR 68.60} \\
\text{C}_{10}\text{H}_{24}\text{PONS.} & \text{Calculated MR 68.79} \\
 & \text{Found \%: P 13.31; 13.22} \\
\text{C}_{10}\text{H}_{24}\text{PONS.} & \text{Calculated \%: P 13.18}
\end{array}
$$

The yield of ester was 2.9 g (63%).

8. O-Hexyl Triethylphosphonamidothioate.   The ester was prepared from 6.4 g of hexyl triethylphosphonamidite and 0.88 g of sulfur. Vacuum distillation of the reaction product from an Arbuzov flask gave O-hexyl triethylphosphonamidothioate, b.p. 132-133° (1.5 mm); d_4^{20} 0.9642; n_D^{20} 1.4790.

$$
\begin{array}{ll}
 & \text{Found MR 78.64} \\
\text{C}_{12}\text{H}_{28}\text{PONS.} & \text{Calculated MR 78.73} \\
 & \text{Found \%: P 11.54; 11.72} \\
\text{C}_{12}\text{H}_{28}\text{PONS.} & \text{Calculated \%: P 11.68}
\end{array}
$$

The yield of the ester was 3.6 g (49.5%).

9. O-Heptyl Triethylphosphonamidothioate. Reaction was between 3.2 g of heptyl triethylphosphonamidite and 0.41 g of flowers of sulfur. Vacuum distillation of the reaction product from an Arbuzov flask gave O-heptyl triethyl-

phosphonamidite, b.p. 137-137.5° (2 mm); d_4^{20} 0.9578; n_D^{20} 1.4789.

	Found MR 82.74
$C_{13}H_{30}PONS.$	Calculated MR 82.65
	Found %: P 10.82; 10.91
$C_{13}H_{30}PONS.$	Calculated %: P 11.10

The yield of ester was 1.15 g (32%).

   10. O-Octyl Triethylphosphonamidothioate.   The ester was prepared from 4.8 g of octyl triethylphosphonamidite and 0.59 g of flowers of sulfur. Vacuum distillation of the reaction product from an Arbuzov flask gave O-octyl triethylphosphonamidothioate, b.p. 144-144.5° (1 mm); d_4^{20} 0.9516; n_D^{20} 1.4793.

	Found MR 87.45
$C_{14}H_{32}PONS.$	Calculated MR 87.27
	Found %: P 10.11; 10.2
$C_{14}H_{32}PONS.$	Calculated %: P 10.37

The yield of ester was 1.8 g (33.4%).

   11- O-Nonyl Triethylphosphonamidothioate.   The ester was prepared from 4.2 g of nonyl triethylphosphonamidite and 0.49 g of flowers of sulfur. Vacuum distillation of the reaction product from an Arbuzov flask gave O-nonyl triethylphosphonamidothioate, b.p. 151-152° (1 mm); d_4^{20} 0.9495; n_D^{20} 1.4796.

	Found MR 91.91
$C_{15}H_{34}PONS.$	Calculated MR 91.88
	Found %: P 9.81 9.78
$C_{15}H_{34}PONS.$	Calculated %: P 10.1

The yield of ester was 1.2 g (25.6%).

   12. O-Decyl Triethylphosphonamidothioate.   The ester was prepared from 4.9 g of decyl triethylphosphonamidite and 0.54 g of flowers of sulfur. Vacuum distillation of the reaction products from an Arbuzov flask gave O-decyl triethylphosphonamidothioate, b.p. 170-172° (1 mm); d_4^{20} 0.9446; n_D^{20} 1.4800.

	Found MR 96.67
$C_{16}H_{36}PONS.$	Calculated MR 96.51
	Found %: P 9.34; 9.45
$C_{16}H_{36}PONS.$	Calculated %: P 9.66

The yield of ester was 1.05 g (19.2%).

III. Action of Ethanol on Triethylphosphonamidous Chloride.

   A mixture of 20 g of triethylphosphonamidous chloride and 50 ml of absolute ether was prepared in a three-necked flask fitted with stirrer, dropping funnel, and reflux condenser. The reaction flask was cooled with snow and salt, and 11 g of ethanol was added to its contents from the dropping funnel over a period of 40 minutes. The reaction was carried out in a current of carbon dioxide. As the alcohol was added, a precipitate formed. It was filtered off at the pump, and the residue, after removal of ether, was vacuum-distilled from an Arbuzov flask, when the following fractions were obtained:

   Fraction I   b.p. to 55° (32 mm);   0.9 g
   Fraction II   b.p. 55-60° (32 mm);   14.1 g
      Residue   0.8 g

Redistillation of Fraction II yielded:

   Fraction I   b.p. to 55° (32 mm);   0.47 g
   Fraction II   b.p. 55-56° (32 mm); 10.5 g
   Fraction III b.p. 56-61° (32-33 mm); 2.7 g

The analysis and constants of Fraction II, b.p. 55-56° (32 mm), showed that it was diethyl ethylphosphonite, d_4^{20} 0.9200; n_D^{20} 1.4215.

Found MR 41.44
$C_6H_{15}PO_2$. Calculated MR 41.39
Found %:P 20.73; 20.68
$C_6H_{15}PO_2$. Calculated%: P 20.65

The crystalline substance was recrystallized twice from alcohol. It was found to be diethylamine hydrochloride (confirmed by analysis for chlorine).

Found %: Cl 32.28; 32.36
$C_4H_{12}NCl$. Calculated%: Cl 32.45

SUMMARY

1. Triethylphosphonamidous chloride and alkyl triethylphosphonamidites (ranging from the methyl to the decyl ester) were synthesized.

2. Triethylphosphonamidothioic chloride was prepared by addition of sulfur to triethylphosphonamidous chloride in presence of aluminum chloride.

3. Alkyl triethylphosphonamidothioates (ranging from the methyl to the decyl ester) were prepared by addition of sulfur to alkyl triethylphosphonamidites.

4. When triethylphosphonamidous chloride was treated with an alcohol, the amido group was eliminated in the form of diethylamine hydrochloride and a dialkyl ethylphosphonite was formed.

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PARACHORS OF TRIALKYLMETHYLSILANES

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In the course of the use of Gibling's group-value method for the calculation of theoretical values of the parachor and the comparison of these values with the experimentally determined values of organic compounds of various types, it has been found necessary to introduce corrections into the theoretical values, these being required— according to Gibling— in order to take account of the interaction of hydrocarbon chains (corrections for parallelism) [1]. Corrections of this sort were found to be necessary for ethers [1, 2], amines [3], and arsines [4], which contain either a polar group ($C = O$, $P = O$, $S = O$), or atoms having unshared electrons, which can cause the bending of ether or hydrocarbon chains in the direction of the central polar group or the atom with the unshared electron pair. After being bent, the chains are arranged parallel to one another, so that a correction for parallelism is required. It would be of interest to determine whether not only compounds of this type, but also compounds of hydrocarbon character— not containing polar groups or atoms having unshared electron pairs—can require parallelism corrections.

Much attention has been given recently to the study of the parachors of hydrocarbons [5]. The value of the parachor has been found to be very sensitive with respect to the structure of a hydrocarbon molecule. Effects due to the presence of side chains and their positions in the hydrocarbon molecule are particularly notable ("strain constant") [6]. All of the experimental results, however, refer to hydrocarbons having short side chains (methyl, ethyl), and for these it is impossible to determine whether the hydrocarbon chains interact and become parallel [5]. In order to resolve the question of corrections for parallelism, instead of hydrocarbons having long chains, such as trialkyl- and tetraalkyl-methanes, we selected the more accessible silanes of analogous structure for investigation. As the parallelism correction is more clearly manifested when three chains rather than four (when paired interactions are possible) are present in the molecule, we prepared a series of trialkylmethylsilanes for the investigation.

Table 1 gives the constants of the compounds that we prepared, the method of preparation being based on that already described for triethylmethylsilane [8] —reaction of trichloromethylsilane with the corresponding organomagnesium compounds.

In the literature there are data on the preparation of compounds No. 1, 2, and 3 of Table 1, but their properties have not been described fully. Compounds No. 1 and 2 were prepared by reaction of the corresponding trialkylfluorosilanes with methyl magnesium iodide the only constant given for No. 1 is b.p. 126.8° (760 mm) [9]. No. 2 is stated to have b.p. 183° (765 mm) and $n_D^{16.5}$ 1.4290, the analytical data being: found% C 69.5; H 14.1; Calculated%: C 69.7; H 14.05 [9]. Tributylmethylsilane (No. 3) was prepared by the action of C_4H_9Li on triethylmethylsilane, and its boiling point is given as 101-104° (9mm) [10].

Data in the literature on the calculation of the parachors of aliphatic hydrocarbons indicate the necessity of making corrections to the values of the molecular parachor for the interaction of side chains, but different corrections are proposed by different investigators. The "strain constant" of Mumford and Phillips is about 3 units for each side chain, and it varies according to the structure of the molecule and the length of the side chain. Gibling finds a correction of -1.7 units for 2,3-dimethylpentane and for 3,4-dimethylhexane and a correction of -1.2 units for 3-ethylpentane [11]. Quayle finds corrections varying from -2.1 to -6.5 units for 17 octane isomers, and in calculations he assumes an average value of -3.7 units for each branching [5].

Table 2 gives values of parachors determined by us for a series of trialkylmethylsilane, beginning from triethylmethylsilane and continuing to tridecylmethylsilane, in which the branching chains are much longer.

The atomic parachors of silicon given in the literature were calculated from the parachors of tetraalkylsilanes [12] and compounds of other classes, and they have nonidentical values ranging from 25.8 to 38.2 units [13]. From the parachor of triethylmethylsilane we have calculated the parachor of the group (C) to be 33.38 units.

$$(C) - Si \diagdown_{\diagdown (C)}^{\diagup (C)}$$
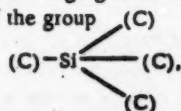
The theoretical values of the parachors were calculated by the "group-value method" both with allowance for the possibility of side-chain interaction (I-between three chains, II- between two chains), and also without such

allowance. In the latter case the discrepancy between observed and calculated parachors exceeded experimental error (it varied from − 0.3% to − 1.5%), which indicates the necessity for corrections to the value of molecular parachor to take into account the parallelism of the chains after the bend at the γ-carbon atom (the correction for the γ-carbon of each chain is − 1.4 units) [14].

The best agreement between observed and calculated parachors was obtained when it was assumed that interaction occurred between two chains of the molecule rather than three, for which considerable discrepancies were observed (from + 0.9% to + 2.1%) (Table 2). The data in Table 2 enable us to conclude that for trialkylmethylsilane molecules the most probable structure is an extended one in which two chains are parallel, which is in accord with data on parachors obtained previously for esters of orthopropionic and various other acids.[15], in which the central atom is not polar.

Quayle [5] has recently proposed that the calculation be based on atomic parachors, and he calculated the parachor of the CH_2 group to be 40.0 units for $\underline{n} < 12$ and 40.3 units for $\underline{n} < 12$. The parachors of trialkylmethylsilanes calculated from Quayle's atomic parachors with a correction for two branchings in the molecule ($-3.7 \times 2 = -7.4$ units) differ appreciably from the observed values, the difference being + 2.5% for triethylmethylsilane, + 1.3% for methyltripropylsilane, still less at + 0.1% for tributylmethylsilane, and then becoming negative until it attains − 0.9 unit for tridecylmethylsilane. Better agreement is therefore obtained between observed and calculated parachors when these are calculated by the group-value method rather than by Quayle's method of atomic parachors.

EXPERIMENTAL

Trialkylmethylsilanes were prepared by the general method of reaction of trichloromethylsilane with the corresponding organomagnesium bromides.

Triethylmethylsilane. Ethylmagnesium bromide was prepared from 16.5 g of magnesium and 75 g of ethyl bromide (added dropwise) in 250 ml of dry ether. The solution so obtained was stirred, and 20 g of trichloromethylsilane, b.p. 66°, was added gradually. Reaction was very vigorous. When the whole of the trichloromethylsilane had been added, the mixture was heated under reflux in a water bath for three hours. Ether was distilled off, and the residue was heated for a further three hours and then decomposed with 10% hydrochloric acid. The acid was added dropwise with the reflux condenser still in place. A little ether was added to the reaction product, and the resulting ethereal solution was washed, first with water, then with sodium carbonate solution, and finally with water again; it was dried over calcium chloride. The ether was distilled off, and the distillation of the residue yielded 6 g of triethylmethylsilane, b.p. $123.0 - 124.0°$ (760 mm). After redistillation over metallic sodium, the trimethylsilane had b.p. 123-124° (760 mm); n_D^{20} 1.4130, d_0^{20} 0.7420. Found MR 43.78; Calculated MR 44.17; γ^{20} 20.82.

Methyltripropylsilane. This was prepared similarly to triethylmethylsilane. Propylmagnesium bromide was prepared in 250 ml of dry ether from 13 g of magnesium and 65 g of propyl bromide, and 20 g of trichloromethylsilane was added immediately to the resulting solution. Reaction began when the mixture was heated in a water bath. The mixture was heated for three hours, and the residue remaining after removal of ether was heated for six hours. Dilute hydrochloric acid was added under ice cooling. The washed and dried product distilled completely (7 g) through a Widmer column at 177-181° (760 mm). After redistillation over sodium the methyltripropylsilane had b.p. 182.5 - 183.5° (765 mm); n_D^{20} 1.4280; d_4^{20} 0.7660; Found MR 57.88; Calculated MR 58.06; γ^{20} 22.90.

In view of their high stabilities, the trialkylmethylsilanes were analyzed by the combustion method. The weighed sample in the boat was covered with a finely ground mixture of cupric oxide and lead chromate, and part of the cupric oxide in the combustion tube was replaced by lead chromate, which was contained in a cartridge of copper gauze. Combustion of trialkylmethylsilanes without the use of lead chromate evidently led to the formation of carbides that could not be broken down by heat [16], and the carbon results for methyltripropylsilane, methyltrioctylsilane, and tridecylmethylsilane were low by 1.5-3.5%, in all analyses, whereas, good agreement was obtained for hydrogen.

$$C_{10}H_{24}Si. \quad \begin{array}{l} \text{Found \%: C 69.73; H 14.11} \\ \text{Calculated\%: C 69.72; H 14.04} \end{array}$$

Tributylmethylsilane. This was prepared in a similar way. The organomagnesium compound was prepared from 10.7 g of magnesium and 60 g of butyl bromide in 180 ml of dry ether, and it was stirred while 20 g of trichloromethylsilane was added rapidly. Reaction occurred with evolution of heat, and when the mixture was heated a precipitate formed. Ether was distilled off, and the residue was heated for five hours in a water bath. The solid precipitate was decomposed with 10% hydrochloric acid, snow cooling being applied. The product was washed with water and sodium carbonate solution, a little ether was added, and the ethereal solution was washed with water and dried with calcium

chloride. The ether was driven off, and the residue was treated with sulfuric acid, washed, diluted with ether, and dried with calcium chloride. The sulfuric acid layer was diluted with water and extracted with ether, and the ether extract was washed and dried over calcium chloride. Vacuum distillation yielded the fractions:

Fraction I   b.p.   64-66° (6.5 mm);   4 g
Fraction II   b.p.   92.5 - 93.5° (5 mm); 13 g

Redistillation of the higher fraction yielded tributylmethylsilane, b.p. 117-118° (17 mm); n_D^{20} 1.4375, d_6^{20} 0.7818, Found   MR 71.92; Calculated   MR 71.95; γ^{20} 24.53.

Found %: C 72.74; H 14.11
$C_{13}H_{30}Si.$ Calculated%: C 72.81; H 14.10

Trihexylmethylsilane.   Trihexylmethylsilane has not been described in the literature. Hexylmagnesium bromide was prepared in 150 ml of dry ether from 7.5 g of magnesium and 50 g of hexyl bromide, b.p. 46-47° (13 mm)(added dropwise) . To the resulting solution 10 g of trichloromethylsilane was added dropwise. The mixture was heated in a water bath for 90 minutes. A precipitate formed on standing. The ether was distilled off, and the precipitate was heated for 5 hours 30 minutes and then cautiously decomposed with 10% hydrochloric acid, which was added dropwise with the reflux condenser in position. The product was washed with water and sodium carbonate solution, and ether was then added. The ethereal solution was washed with water and dried over calcium chloride. The ether was distilled off, and vacuum distillation of the residue through a small Widmer column gave the fractions:

Fraction I   b.p.   105-172.5° (8 mm)
Fraction II   b.p.   172.5-174° (8 mm) (not corrected) — 12.5 g

A second distillation with an Anschütz thermometer yielded a product having b.p. 176.5-177° (9 mm); n_D^{20} 1.4465 d_6^{20} 0.8016; Found MR 99.41; Calculated MR 99.73; γ^{20} 26.75.

Found %: C 76.56; H 14.19
$C_{19}H_{42}Si.$ Calculated%: C 76.43; H 14.18

Methyltrioctylsilane.   Methyltrioctylsilane has not been described in the literature. Octylmagnesium bromide was prepared from 65 g of octyl bromide and 8 g of magnesium, and to the resulting solution 12 g of trichloromethyl-silane was added. Reaction did not begin immediately. A precipitate formed when the mixture was heated for three hours in a water bath. The ether was distilled off, and the residue was heated for eight hours. The reaction product was treated as described above. Much frothing occurred during vacuum distillation. After many fractionations through a small Widmer column, the following fractions were obtained:

Fraction I   b.p. 137-141° (4.5 mm);   4 g
Fraction II   b.p. 205-210° (3 mm);   14.5 g

Redistillation of the higher fraction gave a substance having b.p. 209.5-211° (5 mm); n_D^{20} 1.4520; d_6^{20} 0.8128; Found MR 127.27; Calculated MR 217.51; γ^{20} 28.35.

Found %: C 78.05; H 14.13
$C_{25}H_{54}Si.$ Calculated %: C 78.45; H 14.22

Tridecylmethylsilane.   Tridecylmethylsilane has not been described in the literature. Decylmagnesium bromide was prepared from 66 g of decyl bromide and 7.2 g of magnesium in dry ether, and to the resulting solution 10 g of trichloromethylsilane was added. Reaction occurred without rise in temperature. A precipitate formed when the mixture was heated for three hours in a water bath. After the ether had been removed, the mixture was heated for a further eight hours. The product was decomposed and then treated as described above. Distillation from an Arbuzov flask gave the fractions:

Fraction I b.p. up to 187° (3 mm)
Fraction II b.p. up to 187-215° (3 mm)
Fraction III b.p. up to 215-230° (3 mm)

Fractionation of the fraction boiling up to 187° (3 mm) through a Widmer column gave 6 g of decane, b.p. 62-63°

TABLE 1

No.	Formula	B.p. (°C)	Pressure (mm)	n_D^{20}	d_4^{20}	MR Found	MR Calculated*	γ^{20}
1	(C₂H₅)₃SiCH₃**	123–124	(760)	1.4130	0.7420	43.78	44.17	20.82
2	(n-C₃H₇)₃SiCH₃	182.5–183.5	(765)	1.4280	0.7660	57.88	58.06	22.90
3	(n-C₄H₉)₃SiCH₃	117–118	(17)	1.4375	0.7818	71.92	71.95	24.53
4	(n-C₆H₁₃)₃SiCH₃	176.5–177	(9)	1.4465	0.8016	99.41	99.73	26.75
5	(C₈H₁₇)₃SiCH₃	209.5–211	(5)	1.4520	0.8128	127.27	127.51	28.35
6	(C₁₀H₂₁)₃SiCH₃	261–262.5	(4.5)	1.4565	0.8211	155.0	155.29	29.70

* The molecular refraction was calculated from bond values. The refraction of the C—Si bond was taken as 2,5 units [7].

** Data in the literature b.p. 127° (760 mm), n_D^{20} 1.4160; d_4^{20} 0.7437. MR Found 43.98.

TABLE 2

No.	Formula of Compound	P Found	P Calculated	Correction made	Discrepancy (%)
1	(C₂H₅)₃SiCH₃	374.9	–	–	–
2	(n-C₃H₇)₃SiCH₃	492.2	491.1	3γ − 4.2	+ 0.2
3	(n-C₄H₉)₃SiCH₃	610.3	I 605.2	3γ 3‖ − 10.8	+ 0.8
			II 609.7	3γ 3‖ − 6.4	+ 0.1
4	(C₆H₁₃)₃SiCH₃	847.1	I 834.1	3γ 9‖ − 24.0	+ 1.5
			II 847.5	3γ 3‖ − 10.8	0
5	(C₈H₁₇)₃SiCH₃	1086.7	I 1064.2	3γ 15‖ − 37.2	+ 2.1
			II 1086.6	3γ 5‖ − 15.2	0
6	(C₁₀H₂₁)₃SiCH₃	1322.0	I 1316.3	3γ 21‖ − 50.4	+ 0.4
			II 1326.8	3γ 7‖ − 19.6	− 0.3

(15 mm); n_D^{20} 1.4130. Several fractionations of the higher fractions yielded 12 g of a substance having b.p. 261-262.5° (4.5 mm); n_D^{20} 1.4565; d_0^{20} 0.8211; Found MR 155.0; Calculated MR 155.29; γ^{20} 29.70.

It was not found possible to distil tridecylmethylsilane from a flask fitted with a small Widmer column. The substance distilled only when it was very much overheated (it flowed over the walls in a continuous film).

$$C_{31}H_{66}Si.$$

Found %; C 79.89; H 14.44
Calculated%: C 80.08; 14.31

SUMMARY

1. Trihexylmethyl-, methyltrioctyl-, and tridecylmethyl-silanes, which have not been described previously in the literature, were synthesized.

2. Parachors were determined for 2 series of trialkylmethylsilanes, ranging from triethyl- to tridecyl-methyl-silanes.

3. The parachor data indicate that trialkylmethylsilanes probably have extended structures in which two chains lie parallel, similar to the structure (also derived from parachor data) of orthopropionic esters, in which there is also an absence of any kind of polarity in the central atom.

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NEW METHOD OF PREPARING β-LACTAMS •

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When it had been established that penicillin contains a condensed thiazolidine β-lactam system, various syntheses of lactams of β-amino acids followed. The previously known methods for the preparation of β-lactams — addition of ketones to imines [1-7] or to aromatic nitroso compounds [8], reaction of esters of β-bromo carboxylic acids with imines in presence of zinc [6, 9], and cyclization of β-amino acids, or of their acyl derivatives or esters [6, 10-12] — have been recently supplemented by several new methods: condensation of double acylated aminoacetyl chlorides with various imines and thiazolines [13-18], cyclization of α-haloacyl derivatives of aminomalonic ester in presence of bases [19, 20], and condensation of diazomethane with aryl isocyanates [21, 22].

All of these methods give only limited possibilities for the synthesis of β-lactams, since the ranges of applicability of these reactions are narrow and the starting compounds are generally not readily available. The possibility was not excluded theoretically of the formation of the four-membered β-lactam ring by the action of alkalis on amides of β-halo carboxylic acids:

$$R-ClBr-CH_2 \quad \xrightarrow{-HBr} \quad R-CH-CH_2$$
$$R'-NH-CO \qquad\qquad R'-N-CO$$
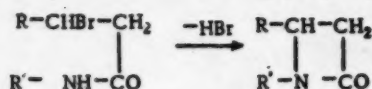
However, elimination of hydrogen halide by the action of alcoholic alkali, by sodamide suspended in absolute ether, by liquid ammonia, and by thermal treatment always yielded amides of the corresponding unsaturated acids (see Tables 1 and 5). It is evident that nucleophilic attack at the β-carbon atom does not occur owing to insufficient electron density on the amide nitrogen atom. The desired course of reaction, therefore, could be ensured only by the selection of the reactants and reaction conditions so that the electron density of the nitrogen atom would be greatly increased. It was natural to make use of solutions of alkali metals or amides of alkali metals in liquid ammonia. Under these conditions the acidity of the amide will be increased and the salt of its imine form will be stabilized. The formation of a salt of this kind should result in a considerable increase in the electron density of the nitrogen atom. In this way the necessary conditions will be created for an attack on the electrophilic β-carbon atom by the nitrogen atom carrying the unshared pair of electrons:

$$RCH-CH_2 \qquad\qquad RCH-CH_2$$
$$R'N=C-O-K^+ \quad \longrightarrow \quad R'N-C=O \quad + KBr$$
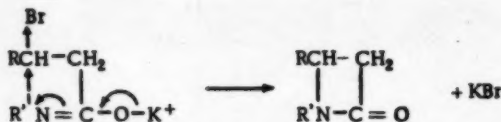
The experimental results were fully in accord with our expectations. When β-chloro- or β-bromo-hydrocinnamanilide was treated with a solution of potassium in liquid ammonia, both hydrocinnamanilide and 1,4-diphenyl-2-azetidinone were formed in good yield. The best results were obtained by the use of solutions of sodamide or potassium in liquid ammonia, the yields of 1,4-diphenyl-2-azetidinone being then almost quantitative.

The investigations showed that the result of the reaction is almost independent of the substituent in the amino group and that amides of β-bromohydrocinnamic acid give higher yields than those of β-chlorohydrocinnamic acid (Table 1).

In this way we succeeded in preparing a series of new N-substituted azetidinones, in which the nitrogen carries not only simple radicals, but also residues of saturated and unsaturated acids:

• This paper is published under the regulations governing "Brief Communications".

TABLE 1

$$C_6H_5CHXCH_2CONHR \nearrow \quad \begin{array}{l} C_6H_5CH=CHCONHR \\[4pt] \underset{R-\ \ N-\ CO}{C_6H_5CH-CH_2} \end{array}$$
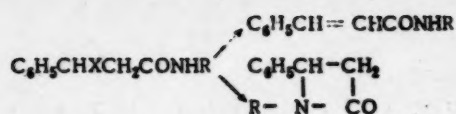
No.	R	X	Reaction conditions	Yield of $C_6H_5CH=CHCONHR$ (%)	Yield of $C_6H_5CH-CH_2$, $R-N-CO$ (%)
1	C_6H_5	Cl	KNH$_2$	–	85•
2	C_6H_5	Cl	NaNH$_2$	–	75
3	C_6H_5	Cl	Solution of potassium in liquid ammonia	–	45••
4	C_6H_5	Cl	Liquid ammonia (a)	74•••	–
5	C_6H_5	Cl	KOH (b)	60	–
6	C_6H_5	Cl	3 hours; suspension of sodamide in benzene	35	–
7	C_6H_5	Br	KNH$_2$	–	94
8	C_6H_5	Br	NaNH$_2$	–	90
9	C_6H_5	Br	Solution of potassium in liquid ammonia	–	63••••
10	C_6H_5	Br	Pyrolysis at 140-150°; 20-minutes	45	–
11	C_6H_{11}	Cl	KNH$_2$	12.8	80
12	C_6H_{11}	Cl	NaNH$_2$	11.7	78
13	C_6H_{11}	Cl	NaOH (b)	88	–
14	$CH_2C_6H_5$	Cl	KNH$_2$	35	65
15	$CH_2C_6H_5$	Cl	KOH (b)	85	–
16	$CH_2C_6H_5$	Br	KNH$_2$	5	88
17	$CH_2CO_2C_2H_5$	Cl	4 days; KNH$_2$	77•••••	2
18	$CH_2CO_2C_2H_5$	Br	4 days; KNH$_2$	29	37•••••
19	$\underset{CH(CH_3)_2}{CHCO_2C_2H_5}$	Br	KNH$_2$	11	69
20	$\underset{CH(CH_3)_2}{CHCO_2C_2H_5}$	Br	Liquid ammonia (a)	86	–
21	$\underset{CH(CH_3)_2}{CHCO_2C_2H_5}$	Br	KOH (b)	89	–
22	$\underset{C(CH_3)_2}{\overset{\parallel}{C}CO_2C_2H_5}$	Cl	KNH$_2$	19	62
23	$\underset{C(CH_3)_2}{\overset{\parallel}{C}CO_2C_2H_5}$	Cl	3 days; liquid ammonia (a)	55	–
24	$\underset{C(CH_3)_2}{\overset{\parallel}{C}CO_2C_2H_5}$	Cl	KOH (b)	73	–
25	$\underset{C(CH_3)_2}{\overset{\parallel}{C}CO_2C_2H_5}$	Br	KNH$_2$	5	75.5

• M.p. 154-154.5° (from alcohol. A mixture with 1,4-diphenyl-2-azetidinone prepared by the condensation of ketene with N-benzylideneaniline [1] melted at the same temperature.

•• In addition to 1,4-diphenyl-2-azetidinone, hydrocinnamanilide was obtained in 34% yield.

••• M.p. 151°, undepressed by admixture of cinnamanilide.

•••• 1,4-Diphenyl-2-azetidinone was accompanied by hydrocinnamanilide in 18% yield.

••••• Under the conditions of the reaction the ester grouping was ammonolyzed and the corresponding amide was obtained.

TABLE 2

$$C_6H_5 - CH - CH_2$$
$$\quad\quad\quad | \quad\quad |$$
$$\quad\quad\quad R - N - CO$$

R	Found			Calculated			Melting point (°C)	Recrystallized from
	C	H	N	C	H	N		
C_6H_{11}	78.28	8.28	6.09	78.6	8.29	6.11	52-53	Heptane
CH_2CONH_2	64.45	5.98	13.64	64.7	5.88	13.72	144-145	Alcohol
$-CHCO_2C_2H_5$ $CH(CH_3)_2$	69.36	7.71	5.12	69.4	7.63	5.09	B.p. 167-170(1 mm)	
$-CCO_2C_2H_5$ $C(CH_3)_2$	70.38	6.78	4.93	70.33	6.96	5.12	51-52	Heptane

TABLE 3

$$C_6H_5CH - CH_2 \quad \xrightarrow{HOH} \quad C_6H_5CH - CH_2COOH$$
$$\quad\quad | \quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad R - N - CO \quad\quad\quad\quad\quad\quad R' - NH$$

R	R'	Reaction conditions	Found				Calculated				M.p. (°C)	Recrystallized from	Yield (%)
			C	H	N	Cl	C	H	N	Cl			
C_6H_5	C_6H_5	One hour at boil with alcoholic solution	74.7	6.29	-	-	74.6	6.23	-	-	134-135*	Ethyl acetate	83
C_6H_{11}	C_6H_5	Ditto	63.89	7.65	4.85	-	63.49	7.76	4.93	-	187-189***	Alcohol-ether	79
$CH_2C_6H_5$	$CH_2C_6H_5$	"	75.04	6.38	5.44	-	75.3	6.66	5.49	-	184-185**	Bicarbonate solution	90
CH_2CONH_2	CH_2CO_2H		66.08	6.07	-	11.83	65.87	6.17	-	12.18	189-190***	-	-
		4 hours at 60-70° with 2 N HCl	59.25	5.90	6.19	-	59.2	5.83	6.28	-	205-206	Water	69
$-CHCO_2C_2H_5$ $CH(CH_3)_2$	$-CHCO_2C_2H_5$ $CH(CH_3)_2$	2.5 hours at 60-70° with 2 N HCl	-	-	3.93	-	-	-	4.26	-	183-185	Alcohol	60
H	$-CCO_2C_2H_5$ $C(CH_3)_2$	1 hour at 90-95° with 20% HCl	53.23	6.05	6.91	18.32	53.59	5.98	6.95	17.67	215-217***	Alcohol-ether	80***

*The literature [23] gives M.p. 134°.

**The literature [12] gives M.p. 187-188°

***Isolated as the hydrochloride

****The literature [24] gives M.p. 217-218°.

TABLE 4

$C_6H_5CHXCH_2CONHR$
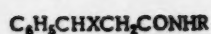
R	X	Found				Calculated				M.p. (°C)	Recrystallized from	Yield (%)
		C	H	N	X	C	H	N	X			
C_6H_5	Cl	69.36	5.50	–	13.25	69.37	5.29	–	13.7	135–135.5	Alcohol	83
C_6H_5	Br	–	–	4.61	–	–	–	4.6	–	125.5–126	Ethyl acetate	85
C_6H_{11}	Cl	–	–	4.81	–	–	–	5.27	–	116–117	" "	79
$CH_2C_6H_5$	Cl	69.46	5.76	–	13.34	70.2	5.85	–	13.0	116–116.5	Alcohol	70
$CH_2C_6H_5$	Br	–	–	4.32	–	–	–	4.4	–	117–118	Ethyl acetate	75
$CH_2CO_2C_2H_5$	Cl	58.78	5.95	–	12.9	57.95	5.98	–	13.17	53–55	Petroleum ether	73
$CH_2CO_2C_2H_5$	Pr	–	–	4.41	–	–	–	4.46	–	82–83	Ethyl acetate	93
$-CCO_2C_2H_5$ | $C(CH_3)_2$	Cl	–	–	4.6	–	–	–	4.52	–	115–116	Alcohol	83
$-CCO_2C_2H_5$ | $C(CH_3)_2$	Br	–	–	3.74	–	–	–	3.95	–	125.5–126	Ethyl acetate	70
$-CHCO_2C_2H_5$ | $CH(CH_3)_2$	Br	–	–	3.64	–	–	–	3.9	–	80–81	Heptane	87

TABLE 5

$C_6H_5CH = CHCONHR$
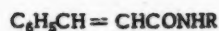
R	Found			Calculated			M.p. (°C)	Recrystallized from
	C	H	N	C	H	N		
C_6H_{11}			5.99			6.1	172–173	Aqueous alcohol
$CH_2C_6H_5$	80.9	6.23		81.01	6.32		103–104 *	Alcohol
CH_2CONH_2	64.69	5.81	13.44	64.7	5.88	13.72	171–172	Alcohol
$-CHCO_2C_2H_5$ | $CH(CH_3)_2$			5.01			5.09	116–117	Aqueous alcohol
$-CCO_2C_2H_5$ | $C(CH_3)_2$			5.12			5.12	164.5–165	Ethyl acetate
$-CCO_2CH_3$ | $C(CH_3)_2$	68.67	6.68	5.39	69.5	6.56	5.4	144–145	Ethyl acetate

* For N-benzylcinnamamide the literature [23] gives m.p. 94 - 96°

$$(CH_3)_2C = \overset{\overset{\displaystyle C_6H_5-CH-CH_2}{|}}{\underset{\underset{\displaystyle COOR}{|}}{C}}-\overset{\displaystyle N}{}-CO$$
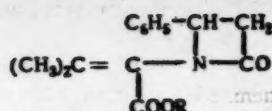
The properties of the new azetidinones are given in Table 2.

The structures of the β-lactams so obtained were proved by their hydrolysis to the corresponding amino acids. The method therefore enables us to pass to β-amino acids and to difficulty accessible mixed amino acids(Table 3):

$$(CH_3)_2CH-\underset{\underset{\displaystyle COOR}{|}}{CH}-\overset{\overset{\displaystyle C_6H_5-CH-CH_2}{|}}{N}-CO \quad\xrightarrow{H_2O}\quad (CH_3)_2CH-\underset{\underset{\displaystyle COOR}{|}}{CH}-\overset{\overset{\displaystyle C_6H_5-CH-CH_2COOH}{|}}{NH}$$
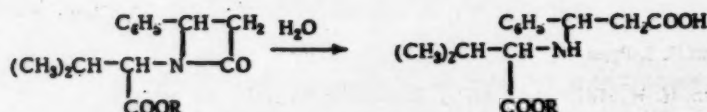
The original amides were prepared in the usual way: the action of amines on β-bromo- and β-chloro-hydrocinnamoyl chlorides• . When β-bromohydrocinnamic acid was treated with the theoretical amount of phosphorus pentachloride, the expected β-bromohydrocinnamoyl chloride was formed, but when β-bromohydrocinnamic acid was heated with excess of thionyl chloride, bromine was quantitatively replaced by chlorine and β-chlorohydrocinnamoyl chloride was formed.

EXPERIMENTAL

β-Chlorohydrocinnamoyl Chloride [1] β-Bromohydrocinnamic acid (20 g) was boiled for two hours with thionyl chloride (30 ml) On the next day excess of thionyl chloride was distilled off, and vacuum distillation of the residue yielded 19.3 g (86%) of β-chlorohydrocinnamoyl chloride, b.p. 130-131° (14 mm).

Found % C 52 59; H 4.01
$C_9H_8OCl_2$. Calculated%: C 53 20; H 3.94

Substituted Amides of β-Chloro- and β-Bromo-hydrocinnamic Acids. A solution of two moles of amine in absolute ether was added dropwise to a stirred ice-cooled solution of one mole of the acid chloride in absolue ether. The precipitate formed was filtered off, washed with water, and recrystallized.

General Method of Preparing β-Lactams. The appropriate β-halohydrocinnamamide (1 mole) was added to a solution of 1 mole of sodamide or potassamide; the mixture was shaken vigorously and set aside overnight. On the next day ammonia was evaporated off at room temperature, and the residue was washed with water. Liquid β-lactams were purified by vacuum distillation, and solid β-lactams were recrystallized from suitable solvents (Table 2).

N-Substituted Cinnamamides. a) An N-substituted β-halohydrocinnamamide was added to liquid ammonia, and the mixture was shaken vigorously and set aside overnight. On the next day ammonia was evaporated off at room temperature, and the residue was washed with water and recrystallized.

b) The appropriate substituted β-halohydrocinnamamide (1 mole) was added to alcoholic alkali (1 mole), and the mixture was allowed to stand for 5-20 minutes at room temperature. Water was then added, and the precipitated crystals were filtered off and recrystallized from suitable solvents (Table 5).

SUMMARY

A method has been devised for the synthesis of β-lactams from amides of β-halo carboxylic acids. Some new azetidinones with residues containing carboxyl groups on the nitrogen have been prepared. The method permits the conversion of β-amino acids into difficulty accessible mixed (secondary) amino acids.

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• The properties of the new amides are given in Tables 4 and 5.

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ACYLATION OF AMINOALKYLPHOSPHONIC AND AMINOALKYLPHOSPHONOTHIOIC ACID

T. Ya Medved and M. I. Kabachnik

In a previous investigation we studied the acylation of aminomethylphosphonic acid [1]. We found that it is more difficult to acylate than its carboxylic analog, glycine. It was considered to be of interest to investigate the acylation of other aminoalkylphosphonic acids and their esters. Moreover, we required N-acyl derivatives of aminoalkylphosphonic acids as starting materials in other investigations.

As we had readily accessible methods at our disposal for the preparation of aminoalkylphosphonic [2] and aminoalkylphosphonothioic [3] acids and their esters, we investigated the acetylation and benzoylation of these compounds. We found that reaction of aminoalkylphosphonic esters with excess of acetic anhydride yielded the corresponding N-acetyl derivatives. Reaction was vigorous: when acetic anhydride was added to an aminoalkylphosphonic ester, the temperature of the reaction mixture rose rapidly to 50-70° and the process was practically complete in 30-40 minutes. When the excess of acetic anhydride was distilled off, the residue usually solidified rapidly, and it was sufficient to recrystallize it once only in order to obtain a pure substance.

Reactions with acetic anhydride yielded diethyl 1-acetamido-1-methylethylphosphonate (I), m.p. 96-97°, and diethyl α-acetamidobenzylphosphonate (II), m.p. 144°. The acylation of an aminoalkylphosphonothioic ester with acetic anhydride proceeded similarly: we prepared O,O-diethyl 1-acetamido-1-methylethylphosphonothioate (III), a colorless substance, b.p. 128-129° (3 mm), which readily solidifies at room temperature and will then melt at 47-48°.

$$
\begin{array}{ccc}
\text{CH}_3\quad\text{PO(OC}_2\text{H}_5)_2 & \text{C}_6\text{H}_5\quad\text{PO(OC}_2\text{H}_5)_2 & \text{CH}_3\quad\text{PS(OC}_2\text{H}_5)_2 \\
\diagdown\,\diagup\,\text{C}\,\diagup & \diagdown\,\diagup\,\text{C}\,\diagup & \diagdown\,\diagup\,\text{C}\,\diagup \\
\text{CH}_3\quad\text{NHCOCH}_3 & \text{H}\quad\text{NHCOCH}_3 & \text{CH}_3\quad\text{NHCOCH}_3 \\
\textbf{(I)} & \textbf{(II)} & \textbf{(III)}
\end{array}
$$
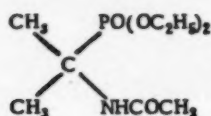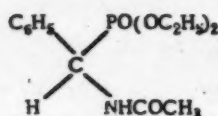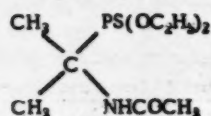
In order to prepare acetyl derivatives of free aminoalkylphosphonic acids by reaction with acetic anhydride it was necessary to heat the reaction mixture under reflux in a boiling water bath for 1-2 hours. When excess of acetic anhydride was distilled from the reaction mixture, the residue rapidly solidified, and the acetyl derivative so obtained could be readily recrystallized.

Reactions with acetic anhydride yielded 1-acetamido-1-methylethylphosphonic acid (IV) and α-acetamidobenzylphosphonic acid (V). Both acids melt with decomposition — the first at 199-200°, and the second at 188°.

$$
\begin{array}{cc}
\text{CH}_3\quad\text{PO(OH)}_2 & \text{C}_6\text{H}_5\quad\text{PO(OH)}_2 \\
\diagdown\,\diagup\,\text{C}\,\diagup & \diagdown\,\diagup\,\text{C}\,\diagup \\
\text{CH}_3\quad\text{NHCOCH}_3 & \text{H}\quad\text{NHCOCH}_3 \\
\textbf{(IV)} & \textbf{(V)}
\end{array}
$$
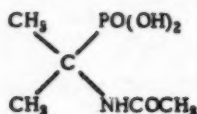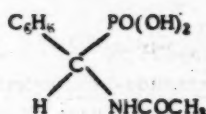
Reaction of aminoalkylphosphonic esters with benzoyl chloride yielded the corresponding N-benzoyl compounds. The reaction was carried out in presence of pyridine, and benzene was used as solvent. Benzoylation of diethyl 1-amino-1-methylethylphosphonate yielded diethyl 1-benzamido-1-methylethylphosphonate (VI), decomposition temperature 105-106°, and reaction with diethyl α-aminobenzylphosphonate yielded diethyl α-benzamidobenzylphosphonate (VII). m. p. 107°.

CH₃ structures at top:

$$\begin{array}{c} CH_3 \quad NHCOC_6H_5 \\ \diagdown \; C \; \diagup \\ \diagup \quad \diagdown \\ CH_3 \quad PO(OC_2H_5)_2 \end{array}$$

(VI)

$$\begin{array}{c} C_6H_5 \quad NHCOC_6H_5 \\ \diagdown \; C \; \diagup \\ \diagup \quad \diagdown \\ H \quad PO(OC_2H_5)_2 \end{array}$$

(VII)
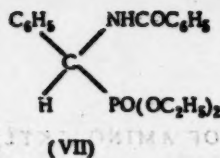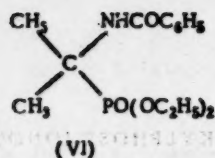
It was found that reaction with p-toluenesulfonyl chloride could be effected in the same way as reaction with benzoyl chloride. Treatment of diethyl 1-amino-1-methylethylphosphonate with p-toluenesulfonyl chloride yielded diethyl 1-methyl-1-p-toluenesulfonamidobenzylphosphonate (VIII), a colorless substance, m.p. 121-123°. Reaction with diethyl α-aminobenzylphosphonate gave diethyl α-p-toluenesulfonamidobenzylphosphonate (IX), a crystalline substance, m.p. 127°:

$$\begin{array}{c} CH_3 \quad NHSO_2C_6H_4CH_3\text{-}p \\ \diagdown \; C \; \diagup \\ \diagup \quad \diagdown \\ CH_3 \quad PO(OC_2H_5)_2 \end{array}$$

(VIII)

$$\begin{array}{c} C_6H_5 \quad NHSO_2C_6H_4CH_3\text{-}p \\ \diagdown \; C \; \diagup \\ \diagup \quad \diagdown \\ H \quad PO(OC_2H_5)_2 \end{array}$$

(IX)
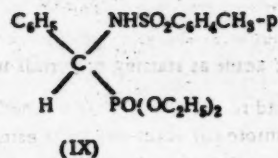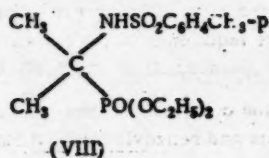
Reaction of benzoyl chloride with free amino acids proceeds most satisfactorily in aqueous alkaline solution under Schotten-Baumann conditions. By this method we obtained 1-benzamido-1-methylethylphosphonic acid (X) and α-benzamidobenzylphosphonic acid (XI):

$$\begin{array}{c} CH_3 \quad NHCOC_6H_5 \\ \diagdown \; C \; \diagup \\ \diagup \quad \diagdown \\ CH_3 \quad PO(OH)_2 \end{array}$$

(X)

$$\begin{array}{c} C_6H_5 \quad NHCOC_6H_5 \\ \diagdown \; C \; \diagup \\ \diagup \quad \diagdown \\ H \quad PO(OH)_2 \end{array}$$

(XI)
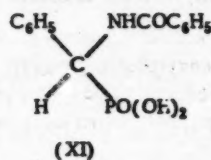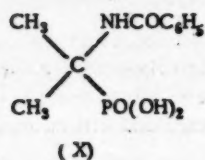
EXPERIMENTAL

Diethyl 1-Acetamido-1-methylethylphosphonate (I). Freshly distilled acetic anhydride (0 76 g) was added to 0.97 of diethyl 1-amino-1-methylethylphosphonate, and the temperature of the mixture rose to 70°. When the temperature fell, the mixture was heated in a boiling water bath for 15 minutes. Excess of acetic anhydride was distilled off under reduced pressure, and the residue in the flask solidified. Recrystallization of the substance from petroleium ether gave 0.74 g (82%) of colorless crystals, m.p. 96-97°.

Found %: C 45.7; 45.5; H 8.5· 9.5; N 6.1; P 13.1; 12.8

$C_9H_{20}NPO_4$. Calculated%: C 45.6; H 8.5; N 5.9; P 13.1

Diethyl α-Acetamidobenzylphosphonate (II). Reaction of 1.22 g of diethyl α-aminobenzylphosphonate with 0.76 g of acetic anhydride gave 0.9 g (63%) of colorless crystals, m.p. 144° (from absolute ethanol).

Found %: C 54.6; 54.9; H 7.2; 7.1; P 10.8; 10.8

$C_{13}H_{20}NPO_4$. Calculated%: C 54.7; H 7.1; P 10.9

O,O-Diethyl 1-Acetamido-1-methylethylphosphonothioate (III). This was prepared from 3.15 g of O,O-diethyl 1-amino-1-methylethylphosphonothioate and 2.28 g of acetic anhydride. Excess of acetic anhydride was removed by distillation at the water pump, and the residue of the reaction mixture was vacuum-distilled from a pear-shaped Claisen flask. A second distillation gave 2.5 g (66%) of a substance having b.p. 116-11 ° (2 mm) and m.p. 47-48°. This substance has an unpleasant odor: it is soluble in organic solvents, but insoluble in water.

Found %: C 42.9; 42.5; H 8.1; 7.9; S 12.3; 12.9; P 12.2; 12.5; N 5.4; 5.3

$C_9H_{20}NPO_3S$. Calculated%: C 42.7; H 7.9; S 12.7; P 12.2; N 5.5

1-Acetamido-1-methylethylphosphonic Acid (IV). A mixture of 3.14 g of 1-amino-1-methylethylphosphonic acid (monohydrate, m.p. 256°) and 15 g of acetic anhydride was heated in a flask under reflux in a boiling water bath until the precipitate present dissolved completely. Acetic anhydride was distilled off under reduced pressure, and the solid residue was recrystallized from methanol, yielding 2.8 g (78%) of colorless crystals, m.p. 199-200°.
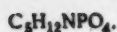
$C_8H_{12}NPO_4$. Calculated %: C 33.1; H 6.7; N 7.7; P 17.1

a-Acetamidobenzylphosphonic Acid (V). The acid (V) was prepared from 1.87 g of a-aminobenzylphosphonic acid and 10 g of acetic anhydride. The procedure was the same as for the acid (IV). Recrystallization from a mixture of methanol and ether gave 1.4 g (60%) of a colorless crystalline substance, m.p.188°.
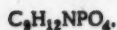
Found %: C 46.8; 46.9; H 5.8; 5.9; N 6.5; 6.4; P 13.6; 13.7

$C_9H_{12}NPO_4$. Calculated %: C 47.2; H 5.3; N 6.1; P 13.5

Diethyl 1-Benzamido-1-methylethylphosphonate (VI). Benzoyl chloride (1.5 g) was added dropwise to a mixture of 1.5 g of diethyl 1-amino-1-methylethylphosphonate, 15 ml of pyridine, and 30 ml of benzene. The resulting mixture was heated for 30 minutes in a bath at 60-70°, and crystals of pyridine hydrochloride were gradually precipitated on the walls of the flask. When cool the mixture was poured into 300 ml of water. the benzene layer wa separated, and the aqueous layer was extracted with 30 ml of benzene. The combined benzene solution was washed with 5% solution of sodium carbonate and dried over sodium sulfate. The benzene was then distilled off, and petroleum ether was added to the residue. The crystals which then precipitated were separated from the solution and recrystallized from absolute ethanol. The product was 1.5 g (65%) of a colorless crystalline substance, m.p. 106°.
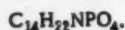
Found %: C 55.9; 55.9; H 7.2; 7.2; N 4.7; 4.8; P10.4; 10.5

$C_{14}H_{22}NPO_4$. Calculated %: C 56.2; H 7.4; N 4.7; P10.3

Diethyl a-Benzamidobenzylphosphonate (VII). The substances taken were diethyl a-aminobenzylphosphonate (1.5 g), pyridine (15 ml), benzene (30 ml), and benzoyl chloride (1.5 g). The treatment of the reaction mixture was as in the preceding experiment. The product was recrystallized from a mixture of benzene and petroleum ether, and 2 g (93.5%) of a colorless crystalline substance, m.p. 107°, was obtained.
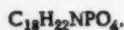
Found %: C 62.1; 62.3; H 6.2; 6.3; N 4.2; 4.1; P 9.0; 9.1

$C_{18}H_{22}NPO_4$. Calculated %: C 62.2; H 6.3; N 4.0; P 8.9

Diethyl 1-Methyl-1-p-toluenesulfonamidoethylphosphonate (VIII). The substances taken were diethyl 1-amino--1-methylethylphosphonate (1.5 g), pyridine (15 ml), benzene (30 ml), and p-toluenesulfonyl chloride (2.5 g). The treatment of the reaction mixture was as in the first experiment. After removal of benzene there remained a brown oily liquid, which solidified when allowed to stand in a desiccator. The product was recrystallized from water, and 0.5 g (13%) of colorless crystals, m.p. 121-123°, was obtained.
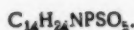
Found %: C 48.0; 48.2; H 6.8; 7.0; S 8.9· 9.1; P 8.8; 8.9

$C_{14}H_{24}NPSO_5$. Calculated %: C 48.1; H 6.9; S 9.2, P8.9

Diethyl a-p-toluenesulfonamidobenzylphosphonate (IX). The substances taken were diethyl a-aminobenzylphosphonate (1.2 g), pyridine (15 ml), benzene (30 ml), and p-toluenesulfonyl chloride (1.5 g). The procedure was as in the preceding experiment. After the benzene had been distilled off, the residue solidified. Recrystallization from 95% alcohol gave 1.5 g (76%) of colorless crystals. m.p. 127°.
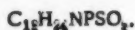
Found %: N 3.5; 3.4; P 7.8; 8.0

$C_{18}H_{24}NPSO_5$. Calculated %: N 3.5; P 7.8

1-Benzamido-1-methylethylphosphonic Acid (X). A solution of 3 g of 1-amino-1-methylethylphosphonic acid in 30 ml of 10% caustic soda solution was stirred and cooled with ice water while 4 g of benzoyl chloride was added gradually at 5-7°. When addition was complete, stirring was continued at the same temperature for about one hour, and then at room temperature for a further period of one hour. The reaction mixture was then cooled with ice water, and concentrated hydrochloric acid was added gradually until the mixture was acid to Congo red. The precipitate that then formed was filtered off, and the filtrate was evaporated under reduced pressure. The precipitate obtained when the mixture was acidified was combined with the residue obtained by the evaporation of the filtrate, and the mixture was dried over calcium chloride, extracted with ether to remove benzoic acid, and then extracted with hot 96% alcohol. Evaporation of the alcoholic solution yielded 2 g (38%) of a colorless crystalline substance, m.p. 197°. From the alcohol-insoluble residue, 0.5 g of unchanged aminoalkylphosphonic acid was isolated.
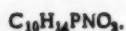
Found %: C 49.5; 49.2; H 5.9; 5.9; N 5.8; 5.6; P 12.6; 12.6

$C_{10}H_{14}PNO_3$. Calculated %: C 49.4; H 5.8; N 5.8; P12.7

a-Benzamidobenzylphosphonic Acid (XI). The substances taken were a-aminobenzylphosphonic acid (3 g). caustic potash (3.6 g made to 25 ml with water), and benzoyl chloride (3 g) The procedure was as in the previous experiment. Recrystallization from water yielded 3 g (64%) of a colorless crystalline substance, m.p. 105-107°. The

substance was obtained as the monohydrate.
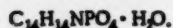
SUMMARY

1. The acylation of aminoalkylphosphonic acids and their esters was investigated. It was shown that they can be acetylated by heating them with acetic anhydride; the free amino phosphonic acids require the more severe conditions.

2. It was shown that aminoalkylphosphonic esters can be benzoylated by heating them with benzoyl chloride in presence of pyridine, and that free aminoalkylphosphonic acids can be benzoylated under Schotten-Baumann conditions.

3. Aminoalkylphosphonic esters react with p-toluenesulfonyl chloride in presence of pyridine with formation of the corresponding p-toluenesulfonyl derivatives.

4. N-Acetyl, N-benzoyl, and N-p-toluenesulfonyl derivatives of aminoalkylphosphonic and aminoalkylphosphono-thioic acids and esters were synthesized and characterized.

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• T.p.= C. B. Translation pagination

METHYLATION OF 1-AMINOALKYLPHOSPHONIC ACIDS AND THEIR ESTERS

T.Ya. Medved and M.I. Kabachnik

We have shown that the amino group of 1-aminoalkylphosphonic acids behaves similarly to the amino group of amino carboxylic acids in various reactions [1]. In particular, it was found [2] that N-alkylation occurs when aminomethylphosphonic acid reacts with dialkyl sulfates in an alkaline medium. Dimethyl sulfate reacts smoothly with aminomethylphosphonic acid with formation of the betaine analog $(CH_3)_3NCH_2PO(OH)\overline{O}$, which we termed a "phosphonobetaine". Diethyl sulfate reacts less readily with aminomethylphosphonic acid, and products of incomplete N-ethylation are formed, as well as the phosphonobetaine. We obtained interesting results in the alkylation of aminomethylphosphonic acid with methyl iodide [1]. When a mixture of these substances was heated in a sealed tube at 200-220° in presence of methanol, the phosphonobetaine iodide

$$(CH_3)_3\overset{+}{N} - CH_2PO(OH)$$
$$I^- \qquad O^-$$
$$(CH_3)_3\overset{+}{N} - CH_2PO(OH)_2$$
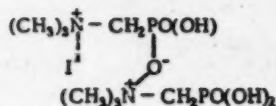
was obtained in good yield, and this substance was converted quantitatively into the phosphonobetaine itself by the action of moist silver oxide. It was thought to be of interest to extend the investigation to the alkylation of other aminoalkylphosphonic acids.

Various aminoalkylphosphonic acids have become readily available as a result of our discovery of a synthesis of 1-aminoalkylphosphonic acids [3] based on reaction between dialkyl hydrogen phosphites, ammonia, and aldehydes or ketones. As new subjects for investigation, we selected 1-amino-1-methylethylphosphonic acid and its ethyl ester, and also α-aminobenzylphosphonic acid. We found that the first of these, like amino-methylphosphonic acid, is methylated in the cold by dimethyl sulfate in weakly alkaline solution, the main reaction product being the corresponding betaine (I):

$$\underset{CH_3}{\overset{CH_3}{>}}C\underset{\overset{+}{N}(CH_3)_3}{\overset{PO(OH)\overline{O}}{<}} \cdot H_2O$$

$$(I)$$
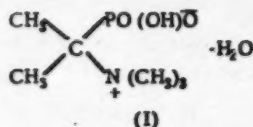
This substance was obtained as colorless crystals of the monohydrate from aqueous alcohol; it melted at 230-231°. It was readily soluble in water, and it titrated as a monobasic acid in presence of alizarin or thymolphthalein as indicator.

An attempt to obtain the same substance by heating 1-amino-1-methylethylphosphonic acid with methyl iodide and methanol in sealed tubes was not successful. When the mixture was heated at 100-130°, the starting materials were recovered unchanged. At higher temperatures deamination of 1-amino-1-methylethylphosphonic acid occurred, and the main reaction product, which was isolated almost quantitatively was tetramethylammonium iodide.

When the diethyl ester of 1-amino-1-methylethylphosphonic acid was taken instead of the acid itself, reaction with methyl iodide occurred much more readily, and heat was not necessary. Thus, when a mixture of diethyl 1-amino-1-methylethylphosphonate with an equimolecular amount of methyl iodide was allowed to stand in a benzene medium for two or three days at room temperature, crystals of diethyl 1-methyl-1-methyl-aminoethylphosphonate hydriodide (II) began to come down:

$$\underset{CH_3}{\overset{CH_3}{>}}C\underset{NHCH_3 \cdot HI}{\overset{PO(OC_2H_5)_2}{<}}$$

$$(II)$$
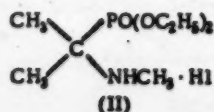
The substance is extremely hygroscopic. It can be crystallized with difficulty from absolute ethanol, and it melts with decomposition at 95°. When this salt was treated with sodium carbonate solution with simultaneous extraction of the phosphonic ester with benzene, free diethyl 1-methyl-1-methylaminoethylphosphonate (III) was obtained, after drying the extract with sodium sulfate, as a mobile liquid, b.p. 77-81° (4 mm):

$$CH_3, CH_3 \diagup C \diagup PO(OC_2H_5)_2, NHCH_3$$

(III)
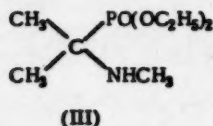
When the alkylation of diethyl 1-amino-1-methylethylphosphonate was carried out under the same conditions with two molecular proportions of methyl iodide, instead of one, a mixture of substances differing in extent of methylation was formed (mono- and di-methyl derivatives), and we did not succeed in separating this mixture.

1-Amino-1-methylethylphosphonic acid can be most readily methylated with the aid of formaldehyde and formic acid. We found that, when a mixture of 1-amino-1-methylethylphosphonic acid, formaldehyde, and formic acid was heated in a boiling water bath, 1-dimethylamino-1-methylethylphosphonic acid (IV) was formed:

$$CH_3, CH_3 \diagup C \diagup PO(OH)_2, NH_2 + 2CH_2O + 2HCOOH = CH_3, CH_3 \diagup C \diagup PO(OH)_2, N(CH_3)_2 + 2H_2O + 2CO_2$$

(IV)
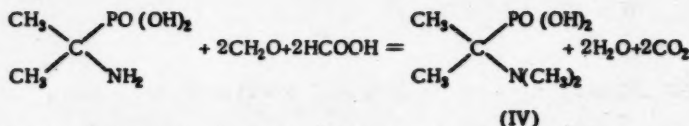
Reaction was complete in 5-6 hours, and a yield of about 80% was obtained. The compound is a crystalline substance, and it can be recrystallized from aqueous alcohol; it melts with decomposition at 256°. It titrates as a monobasic acid when phenolphthalein is used as indicator.

Attempts to bring about the addition of methyl iodide to the above N,N-dimethyl compound with the object of obtaining a fully methylated product did not give the expected result. At temperatures of up to 130-140° the starting materials were recovered unchanged, and at still higher temperatures, the compound was deaminated. An attempt to bring about addition of methyl iodide by long shaking at room temperature of a mixture of an ethereal solution of methyl iodide and an aqueous alkaline solution of 1-amino-1-methylethylphosphonic acid was also unsuccessful.

We also carried out the methylation of α-aminobenzylphosphonic acid with formaldehyde and formic acid. Reaction was complete after 2-3 hours' heating in a water bath, and a 26% yield of α-dimethylaminobenzylphosphonic acid (V), m.p. 230° was obtained:

$$C_6H_5, H \diagup C \diagup PO(OH)_2, N(CH_3)_2$$

(V)
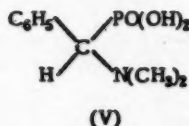
Thus, for the preparation of monomethyl derivatives of 1-aminoalkylphosphonic acids, reaction of their esters with methyl iodide can be used. For the preparation of dimethyl derivatives, the acids can be treated with formaldehyde and formic acid. Finally, the amino phosphonic acids can be converted into fully methylated derivatives by reaction with dimethyl sulfate in aqueous alkaline solution.

EXPERIMENTAL

1-Amino-1-methylethylphosphonic Acid Trimethylbetaine (I). A solution of 8.7 g of 1-amino-1-methylethylphosphonic acid in 75 ml of water was rendered alkaline to phenolphthalein. Dimethyl sulfate (32 g) was added slowly to the solution, and throughout the whole experiment (4-5 hours) the alkalinity of the medium was maintained. When reaction was complete, the mixture was heated in a boiling water bath for one hour, neutralized with sulfuric acid, and evaporated down on a water bath. The residue was extracted with boiling 95% alcohol. The alcohol extract was evaporated, and the residue was again extracted with alcohol. In this way

the substance was freed from potassium methyl sulfate. The residue from the last extract was dissolved in a little water, dilute acid (1 : 1) was added, and the solution was boiled on a gauze for three hours in order to decompose residual methyl hydrogen sulfate. Sulfuric acid was then precipitated with barium chloride (acid medium), and the filtrate was evaporated on a water bath. The residue was again extracted with 95% alcohol, and the alcohol was evaporated from the extract. The substance remaining after removal of alcohol (the chloride of the methylated product) was dissolved in a little water, and excess of freshly precipitated silver oxide was added to the solution. The solution was heated in a water bath and filtered. Hydrogen sulfide was passed through the filtrate, silver sulfide was filtered off, and the new filtrate was evaporated on a water bath. The residue was recrystallized from aqueous alcohol (40 ml of alcohol and 15 ml of water). The crystals that came down after two days were dried in a vacuum desiccator over phosphoric oxide. The product, which was obtained as the monohydrate and amounted to 3 g (27%), melted with decomposition at 230-231°.

<div align="center">

Found %: C 35.9; 35.9; H 9.0; 9.1; N 7.0; 7.1; P 15.5; 15.8

$C_6H_{17}NPO_3 \cdot H_2O$. Calculated %: C 36.2;   H 9.1;   N 7.0;   P 15.6

</div>

Its aqueous solution was acid to litmus. It titrated as a monobasic acid against 0.1 N NaOH when alizarin or thymolphthalein was used as indicator:

<div align="center">

Equivalent found: 199.0 (with alizarin)

198.0 (with thymolphthalein).

Equivalent calculated for $C_6H_{17}NPO_3 \cdot H_2O$: 199.2.

</div>

Methylation of 1-Amino-1-methylethylphosphonic Acid with Methyl Iodide. 1-Methyl-1-methylamino-ethylphosphonic Acid. When 1-amino-1-methylethylphosphonic acid was heated with methyl iodide and methanol at 170° and higher, tetramethylammonium iodide and phosphoric acid were formed. A mixture of 1 g of 1-amino-1-methylethylphosphonic acid, 3 ml of methyl iodide, and 3 ml of methanol was heated for six hours at 100° in a sealed glass tube. Excess of methyl iodide and methanol was distilled from the dark-colored liquid obtained, and a nondistilling sirupy residue remained. This was dissolved in a little water, treated with an excess of freshly precipitated silver oxide, and filtered. The filtrate was saturated with hydrogen sulfide, silver sulfide was removed, and the aqueous filtrate was evaporated on a water bath. The thick sirupy residue, after being vacuum dried over phosphoric oxide and rubbed out with dry ether, was converted into a powder, which was recrystallized from absolute alcohol. The crystallization, which was extremely slow (about three days at 20°) yielded 0.3 g of very hygroscopic colorless crystals, m.p. 140°.

<div align="center">

Found%: N 9.2; 9.1; P 20.2; 20.3

$C_4H_{12}NPO_3$. Calculated%: N 9.2;   P 20.3

</div>

Diethyl 1-Methyl-1-methylaminoethylphosphonate Hydriodide (II). Methyl iodide (1.42 g) was added to a solution of 1.95 g of diethyl 1-amino-1-methylethylphosphonate in 10 ml of dry ether, and the mixture, contained in a closed flask, was placed in the dark at room temperature. Crystals gradually appeared on the walls of the flask. After six days the solid present was separated from the solution and recrystallized from a mixture of absolute alcohol and ether, when 0.6 g of colorless crystals, m.p. 95°, was obtained. This substance is extremely hygroscopic. It is readily soluble in water, methanol, and ethanol, but insoluble in ether.

<div align="center">

Found %: C 28.1; 28.2; H 6.3; 6.4; N 4.9; 4.7; P 10.0; 9.8

$C_8H_{21}PNIO_3$. Calculated %: C 28.5 ;   H 6.2;   N 4.2;   P 9.2

</div>

Diethyl 1-Methyl-1-methylaminoethylphosphonate (III). Methyl iodide (5.7g) was added to a solution of 7.8 g of diethyl 1-amino-1-methylethylphosphonate in 30 ml of ether, and the mixture was set aside for five days. The crystals formed were separated from the liquid and then treated with 5% aqueous NaOH and ether. The ether layer was separated from the aqueous layer, which was extracted with a fresh portion of ether. The combined ether extracts were dried with sodium sulfate. The residue after removal of ether was vacuum-fractionated, and a fraction, amounting to 2.9 g (35%) and boiling at 77-81° (4 mm) was collected. It was slightly yellowish clear mobile liquid having n_D^{19} 1.4370; d_4^{20} 1.0193. Found: MR 53.6. Calculated: MR 53.7.

Found %: N 6.3; 6.3; P 15.0; 15.0

$C_8H_{20}NPO_3$. Calculated %: N 6.7;   P 14.8

1-Dimethylamino-1-methylethylphosphonic Acid (IV).   A mixture of 3.9 g of 1-amino-1-methylethyl-phosphonic acid, 4.4 g of 40% formaldehyde solution, and 3.4 g of 77% formic acid was heated in a flask under reflux in a boiling water bath. There was a brisk evolution of carbon dioxide, which gradually slowed down and stopped completely after eight hours. The mixture was then heated at 125° for 40 minutes. The reaction mixture was evaporated down, and the solid residue was recrystallized from 70% alcohol. The product was 3.3 g (79.6%) of colorless crystals, readily soluble in water, but insoluble in ether, benzene, and other organic solvents. Aqueous solutions of the substance are acid to litmus and it can be titrated as a monobasic acid in presence of phenolphthalein as indicator. The substance melts with decomposition at 220-223°.

Found %: C 36.0; 36.1; H 8.4; 8.2; N 8.5; 8.4; P 18.7; 18.6

$C_5H_{14}NPO_3$. Calculated %: C 35.9;   H 8.4;   N 8.4;   P 18.6

Values of 168.9 and 166.6 were found for the equivalent weight, determined by titration with 0.1 N NaOH to phenolphthalein; the calculated equivalent weight is 167.

a-Dimethylaminobenzylphosphonic Acid (V). A mixture of 2.5 g of a-aminobenzylphosphonic acid, 2 g of 40% formaldehyde, and 1.6 g of 77% formic acid was heated in a flask under reflux in a boiling water bath. Evolution of carbon dioxide ceased after 2 hours 30 minutes. The liquid part of the reaction mixture was then distilled off under reduced pressure, and the residual hygroscopic solid was dried in a desiccator and dissolved in 3 ml of absolute alcohol. Alcoholic aniline (2 ml of alcohol and 4 ml of aniline) was added to the solution. The crystals of the aniline salt which had separated by the next day were filtered off and re-crystallized twice from 95% ethanol. In the course of this treatment the salt was freed from aniline. The product, amounting to 0.8 g (26%), was a crystalline substance, melting with decomposition at 230°.

Found %: N 6.6; 6.5; P 14.3; 14.4

$C_9H_{14}PNO_3$. Calculated %: N 6.5;   P 14.4

An aqueous solution of the substance was titrated with 0.1 N NaOH to phenolphthalein, and a value of 225 was found for the equivalent weight (calculated value 215).

SUMMARY

1. The alkylation of 1-aminoalkylphosphonic acids and their esters was investigated.

2. It was shown that the reaction of 1-aminoalkylphosphonic esters with methyl iodide can be used for the preparation of monomethyl derivatives; dimethyl derivatives can be prepared by the smooth reaction that occurs with formaldehyde and formic acid; and for the preparation of fully methylated 1-aminoalkyl-phosphonic acids, reaction with dimethyl sulfate in aqueous alkaline solution can be used.

3. The following substances were prepared and characterized: 1-amino-1-methylethylphosphonic acid trimethylbetaines; diethyl 1-methyl-1-methylaminoethylphosphonate hydriodide; 1-dimethylamino-1--methylethylphosphonic acid; and a-dimethylaminobenzylphosphonic acid.

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*T.p. = C.B. Translation pagination.

REFORMING OF TUIMAZIN GASOLINE IN CONTACT WITH TROSHKOV KAOLIN

N.I. Shuikin and E.A. Timofeeva

We have studied the catalytic properties of Troshkov kaolin under the conditions applying in the refining of the middle fraction (170-300°) from the primary tar of Budagov sapropelites [1], in the desulfurizing of various gasolines [2], and in the transformations of individual hydrocarbons of various classes [3-5]. It was shown in these investigations that Troshkov kaolin has many valuable catalytic properties: ability to bring about the cracking, isomerization, alkylation, and dehydrocyclization of hydrocarbons, disproportionation of hydrogen, and also desulfurization.

In the present investigation our object was to explore the possibility of effecting a substantial increase in the octane number of Tuimazin gasoline by bringing it into contact with activated Troshkov clay at atmospheric pressure. As the result of experiments on the reforming of the whole gasoline in contact with the clay, and also of the same gasoline after the separation of detonating centers (n-alkanes), we succeeded in finding conditions under which the octane rating of the gasoline was considerably increased — up to 72.0 and 76.8 in presence of 1.5 ml of ethyl fluid (TEL, i.e. tetraethyllead).

EXPERIMENTAL

The experiments on the reforming of gasoline were carried out in the usual flow-type apparatus at 500° at a space velocity of 0.3 hr^{-1}. The contents of sulfonatable compounds were determined by treating the original gasoline and the catalyzates with 2% oleum; their iodine numbers were determined by the Margosches method [6]; sulfur contents by the lamp method [6], and octane numbers by the motor method. The composition of the kaolin is given in one of our previous papers [1]. The clay was activated with sulfuric acid.

The properties of the original Tuimazin gasoline are given in Table 2.

Catalytic Treatment of Tuimazin Gasoline in presence of Activated Troshkov Clay

A head fraction boiling up to 66° (18% by weight) was separated from the original gasoline by fractionation through a 20-plate column. The gasoline, freed from the head fraction, was subjected to reforming in contact with activated Troshkov clay [100 ml (73.0 g) of catalyst, layer 360 mm in length catalysis tube diameter 18 mm] at 500° at a space velocity of 0.3 hr^{-1}. Altogether, 1200 ml (887 g) of gasoline was passed over the catalyst (without its being regenerated). After the catalyst had been regenerated, 300 ml (196 g) of the head fraction of the gasoline was passed over the catalyst at 400° and at the same space velocity. From 100 ml of gasoline 3.27 liters of gas was obtained, and this contained 22.9% of unsaturated hydrocarbons, 12.3% of hydrogen, and 64.8% of alkanes. Table 1 gives the properties of the original head fraction and gasoline freed from head fraction, and also of the catalyzates derived from these.

The catalyzates from the two gasoline fractions were mixed in the appropriate proportions. The properties of the gasoline so obtained are given in Table 2.

Thus, as the result of the catalytic treatment of Tuimazin gasoline in presence of activated Troshkov clay, the sulfur content is reduced by a factor of 18.5 and the fractional composition is improved. The octane number of gasoline with 1.5 ml of TEL is increased by 19.5. The group composition of the gasoline is changed: the content of aromatic hydrocarbons is increased by 11%, the content of cyclohexane hydrocarbons is reduced by one-half, the content of cyclopentane hydrocarbons is increased somewhat, and the content of alkanes is reduced.

Reforming of Tuimazin Gasoline in Contact with Activated Troshkov Clay after Prior Removal of Detonating Centers

The whole gasoline was distilled through a 20-plate column and 6° fractions containing n-alkanes were separated. From 6544.6 g of gasoline we obtained:

1) Fractions containing n-alkanes . . . . 1486.2 g
      including:

    Hexane fraction   66.0 − 72.0° . . . . 268.4 g
    Heptane   "   95.0 − 101.0° . . . . 402.9 g
    Octane   "   122.5 − 128.5° . . . . 341.3 g
    Nonane   "   148.0 − 154.0° . . . . 300.0 g
    Decane   "   171.0 − 178.0° . . . . 173.6 g

2) Gasoline without detonating centers . . . . 4956.4 g
    including the head fraction . . . . 699.1 g

3) Losses . . . . 102.0 g

From the fractions containing n-alkanes, aromatic hydrocarbons and sulfur compounds were separated by adsorption on silica gel. These fractions were then fractionated through a 70-plate column. The properties of the n-alkane concentrates then obtained are given in Table 3.

The data in Table 3 show that the properties of the n-alkane concentrates obtained from the gasoline are fairly close to those of the corresponding pure hydrocarbons.

TABLE 1

Properties of Distillates from the Original Gasoline and their Catalyzates

Gasoline	n_D^{20}	d_4^{20}	Sulfur content (%)	Sulfonatable hydrocarbons (% by vol.)
Original gasoline freed from head fraction	1.4193	0.7491	0.141	12.0
Its catalyzate	1.4230	0.7519	0.009	22.5
Head fraction	1.3710	0.6537	0.121	−
Its catalyzate	1.3720	0.6446	0.011	−

The gasoline without the n-alkanes and the head fraction was subjected to reforming in contact with activated Troshkov clay at 500° at a space velocity of 0.3 hr⁻¹. Over 100 ml of catalyst, 944 ml (698.6 g) of gasoline was passed; the catalyst was not regenerated. The head fraction was treated separately at 400° at the same velocity. The catalyzates were mixed to give the gasoline whose properties are presented in Table 2. Thus, as a result of the refining of the gasoline by this method its octane number was increased by 18.7 units in absence of TEL and by 24.3 units in presence of 1.5 ml of TEL. The amount of aromatic hydrocarbons was increased by 13% by volume, the sulfur content suffered a sevenfold reduction, and the content of low-boiling fractions was increased. There can be no doubt that, if required, n-alkanes could be prepared from Tuimazin gasoline in a higher degree of purity.

Effect of Thermal Treatment on the Properties of Tuimazin Gasoline

In order to determine the effect of a purely thermal treatment on the properties of the gasoline, 500 ml of the whole Tuimazin gasoline was passed at 500° and at the same velocity as in the catalytic reforming experiments through the catalysis tube filled with glass wool. The resulting gasoline, obtained in 89.0% yield, had n_D^{20} 1.4144 and d_4^{20} 0.7403, contained 0.09% of sulfur and 13.5% of sulfonatables, and had an iodine number of 8.2 and an octane number of 62.0 in presence of 1.5 ml of TEL. Thus, one thermal treatment on Tuimazin gasoline has a lower refining effect than contact with Troshkov kaolin under the same conditions.

SUMMARY

1. The conditions were determined for the catalytic refining of Tuimazin gasoline in presence of activated Troshkov kaolin.

2. After direct contact of Tuimazin gasoline with Troshkov kaolin = 300°, the octane number of the gasoline was increased from 37.3 without TEL/52.4 with 1.5 ml of TEL to [...]/[...] with 1.5 ml TEL.

3. Reforming under similar conditions of gasoline from which part of the n-alkanes has been removed yields a gasoline having an octane number of 56.0 without TEL and 76.8 with 1.5 ml TEL.

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TABLE 2

Yield (% on original gasoline)	n_D^{20}	d_4^{20}	Sulfur content (%)	Iodine number	Sulfonatable hydrocarbons (% by volume)	Octane number without TEL	Octane number with 1.5 ml of TEL	Beginning of boiling	10 ml	30 ml	50 ml	98 ml	Residue and losses (ml)	Aromatic hydrocarbons	Cyclopentane hydrocarbons	Cyclohexane hydrocarbons	Alkanes
Original gasoline																	
—	1.4193	0.7390	0.185	2.2	10.0	37.3	52.5	60	84	107	130	200	2	12.0	13.9	12.7	61.4
Gasoline obtained by refining in presence of activated Troshkov clay																	
87.2	1.4180	0.7430	0.010	0.0	—	—	72.0	58	90	110	127	194	2	23.0	15.3	6.6	55.1
Gasoline obtained by removal of detonating centers and then reforming in contact with activated Troshkov clay																	
84.1*	1.4200	0.7391	0.027	1.2	23.0	56.0	76.8	38	70	92	124	195	2	—	—	—	—

* Including 76.0% of gasoline and 7.5% of n-alkanes

TABLE 3

Properties of n-Alkane Concentrates Separated from Tuimazin Gasoline

n-Alkane	B.p. (°C) corrected	Properties of concentrates n_D^{20}	d_4^{20}	Yield (% by volume on original gasoline)	Properties according to literature [7] n_D^{20}	d_4^{20}	B.p. (°C, corrected)
Hexane	68.2-69.2	1.3765	0.6609	2.0	1.37506	0.65942	68.8
Heptane	98.0-99.0	1.3890	0.6849	2.8	1.38774	0.68375	98.4
Octane	125.0-126.0	1.4025	0.7103	1.7	1.39764	0.70283	125.6
Nonane	150.3-151.3	1.4091	0.7197	0.6	1.40562	0.71790	150.7
Decane	173.6-174.6	1.4162	0.7312	0.4	1.41205	0.72985	174.0

SUMMARY

1. The conditions were determined for the catalytic refining of Tuimazin gasoline in presence of activated Troshkov kaolin.

2. After direct contact of Tuimazin gasoline with Troshkov kaolin at 500°, the octane number of the gasoline was increased from 37.3 without TEL (52.5 with 1.5 ml of TEL) to 72.0 with 1.5 ml of TEL.

3. Reforming under similar conditions of gasoline from which part of the n-alkanes has been removed yields a gasoline having an octane number of 56.0 without TEL and 76.8 with 1.5 ml of TEL.

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• T.p. = C.B. Translation pagination.

REACTIONS OF 3,3,4-TRIMETHYL-2-PENTANOL

A.P. Meshcheryakov and L.V. Petrova

With the object of preparing 2,3,3-trimethylpentane from 3,3,4-trimethyl-2-pentanol, we studied the reactions of this alcohol under the conditions of hydrogenational catalysis, and also of its acetic ester under pyrolysis conditions. In hydrogenational catalysis at 100-120 atm and 280-290°, dehydration of the alcohol is accompanied by isomerization, and the main product is 2,3,4-trimethylpentane with only a small amount of 2,3,3-trimethylpentane:
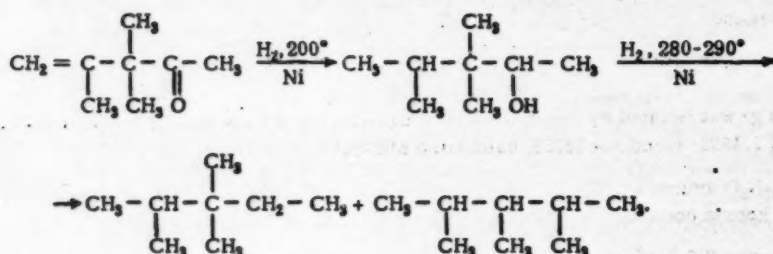
When hydrogenation is carried out over a nickel catalyst precipitated on silica gel at 100-120 atm and 280-290°, demethylation occurs:
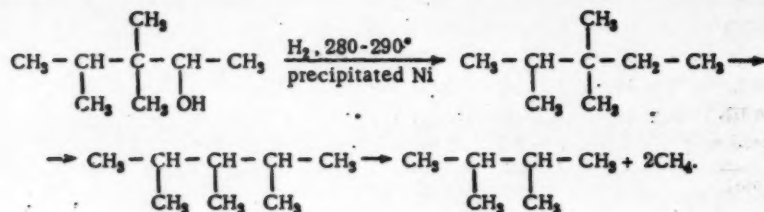
Our experiments on the dehydration of 3,3,4-trimethyl-2-pentanol with acetic anhydride in presence of anhydrous sodium acetate by the method of Hickinbottom and Porter [1] showed that the dehydration of this secondary alcohol does not go, even after long boiling (48 hours).

According to various investigations [2-6], pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol should yield only 3,3,4-trimethyl-1-pentene, but it was found that, in the pyrolysis of the acetic ester of this highly ramified alcohol, isomerization again occurred, and a mixture of two isomers was obtained: 2,3,4-trimethyl-1-pentene and 3,3,4-trimethyl-1-pentene. Only by the Grignard synthesis did we succeed in preparing 2,3,3-trimethylpentane in the pure state.

EXPERIMENTAL

3,3,4-Trimethyl-2-pentanol was prepared by the hydrogenation of 3,3,4-trimethyl-4-penten-2-one, which was synthesized from 2,3-dimethyl-2-butene and acetic anhydride in presence of zinc chloride:
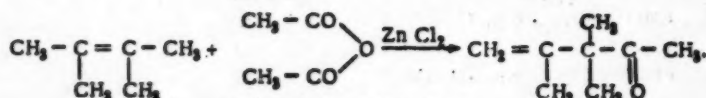
2,3-Dimethyl-2-butene was prepared by the dehydration of pinacol at 200-220° over a catalyst (20% of

969

zinc chloride on a pumice carrier) at a space velocity of $0.2 \ hr^{-1}$. The crude olefin was separated from water, dried over calcium chloride, and fractionated through an 18-plate column. The yield was 60%. The constants of the 2,3-dimethyl-2-butene were b.p. 70-73°; d_4^{20} 0.7007; n_D^{20} 1.4050; found MR 29.44; calculated MR 29.36.

The ketone was synthesized by Kondakov's method [7] under the conditions described in Mesncheryakov and Petrova's paper. 2,3-Dimethyl-2-butene (35 g) and acetic anhydride (42.5 g) were introduced simultaneously into a 250-ml round-bottomed flask having two side openings. The reaction was carried out at 20-30° for eight hours with constant stirring. The reaction flask was then cooled with ice, and the reaction product was decomposed with cold water. The upper layer was separated, washed (with water, with saturated sodium carbonate solution, and again with water), dried over calcium chloride, and fractionated from a Favorsky flask. The product had a strong camphor odor. The amount of the product taken for fractionation was 49 ml, and the following fractions were obtained:

Fraction I,	b.p. 63-140°;	9 ml
Fraction II,	b.p. 142-153°;	30 ml
Fraction III,	b.p. 153-165°;	4 ml
Residue		5 ml
Total		48 ml

The ketone $C_8H_{14}O$ (25 g) was isolated by fractionation through an 18-plate column. Its constants were b.p. 145-150°; d_4^{20} 0.8541; n_D^{20} 1.4321; found MR 38.26; calculated MR 38.64.

Its semicarbazone $C_9H_{17}N_3O$ melted at 150-152°, in accord with the data of Colonge and Mostafavi [8]. It was found that the yield of ketone could be increased to 69.3% by carrying out the synthesis at 0°.

With the object of preparing 2,2,3-trimethylpentane, the 3,3,4-trimethyl-4-penten-2-one that we had prepared was hydrogenated at 200° at 100-120 atm in an autoclave over a mixed catalyst (15 g of alumina and 30 g of A.A. Bag's nickel catalyst). For the hydrogenation, 50 g of the ketone and 15% of nickel catalyst + 15% of alumina were taken, and 45 ml of hydrogenation product was obtained, the fractionation of which gave the following fractions:

Fraction I,	b.p. 50-150°;	Traces
Fraction II,	b.p. 150-164°;	2 ml
Fraction III,	b.p. 164-166.5°;	40 ml
Residue		2 ml
Total		44 ml

The main hydrogenation product b.p. 164-166.5°, was found to be 3,3,4-trimethyl-2-pentanol, d_4^{20} 0.8557; n_D^{20} 1.4381; found MR 39.38; calculated MR 39.56. The hydroxyl content was determined by the Chugaev-Tserevitinov method.

Found % OH 12.0
$C_9H_{18}O$. Calculated % OH 13.1

At 200°, therefore, hydrogenation of the unsaturated ketone goes only as far as the alcohol.

In order to obtain 2,3,3-trimethylpentane, the 3,3,4-trimethyl-2-pentanol was hydrogenated over the same catalyst, but at 280-290°. The hydrogenation product was extracted from the autoclave with ethanol, which was then removed by repeated washing with water. The hydrocarbon was separated, dried over calcium chloride, and fractionated over sodium through an 18-plate column, 20 ml being taken for the fractionation:

Fraction I,	b.p. up to 112°;	3.5 ml
Fraction II,	b.p. 112-113.8°;	2.0 ml
Fraction III,	b.p. 113.8-114.8°;	12.0 ml
Fraction IV,	b.p. 115-129.0°;	2.3 ml
Total		19.8 ml

Refractionation of the 113.8-114.8° and 112-113.8° fractions over sodium gave the fractions:

Fraction I,	b.p. up to 113.6°;	2.2 ml	
Fraction II,	b.p. 113.8-114.8°;	10.0 ml	
Fraction III,	b.p. 115-120°;	0.8 ml	
	Total	13.0 ml	

The hydrocarbon had b.p. 113.8-114.8°; d_4^{20} 0.7218; n_D^{20} 1.4060; found MR 38.86; calculated MR 39.14.

The structure of the hydrocarbon obtained was established by Raman spectrum analysis. It was found that isomerization had occurred during the hydrogenation process, and instead of only the expected 2,3,3-trimethylpentane, 2,3,4-trimethylpentane was formed in predominating amount together with some 2,3,3-trimethylpentane.

When 3,3,4-trimethyl-2-pentanol was hydrogenated at 100-120 atm and 280-290° over a nickel catalyst precipitated on silica gel, the main fraction of the resulting catalyzate had b.p. 56-58°; n_D^{20} 1.3950; d_4^{20} 0.6750; found MR 29.07; calculated MR 29.90.

The Raman spectrum showed that the 56-58° fraction consisted almost entirely of 2,3-dimethylbutane. Under these conditions, therefore, the hydrogenation product 2,3,3-trimethylpentane is demethylated to 2,3-dimethylbutane.

With the object of preparing 2,3,3-trimethylpentane by the hydrogenation of 3,3,4-trimethyl-1-pentene, we carried out experiments on the preparation of 3,3,4-trimethyl-1-pentene by the thermal degradation of the acetic ester of 3,3,4-trimethyl-2-pentanol by Hickinbottom's method. The acetic ester was prepared by Spassow's method [9]:

$$2C_8H_{17}OH + 2CH_3COCl + Mg = MgCl_2 + H_2 + 2C_{10}H_{20}O_2$$
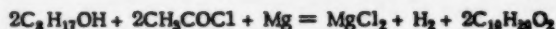
A mixture of 6 g of magnesium, 25 g of 3,3,4-trimethyl-2-pentanol (dried with potassium carbonate and twice distilled over sodium), and 50 g of absolute ether was prepared in a 500-ml round-bottomed flask. The mixture was shaken while a solution of 27.3 g of acetyl chloride in 50 ml of absolute ether was added from a dropping funnel. When the whole of the acetyl chloride had been added, the reaction mixture was set aside in a bath of cold water for one hour and was then heated at 40-50° for two hours. The solid reaction product was cooled with ice water and decomposed with a cooled potassium carbonate solution (20 g of potassium carbonate in 250 ml of water). The mixture was extracted with three successive 35-ml portions of ether, and the ether extracts were dried over calcium chloride. The ether was distilled off through an 18-plate column, and the acetic ester was dried over sodium sulfate. The yield of acetic ester was 58.6%.

Th acetic ester $C_{10}H_{20}O_2$ was vacuum-fractionated twice. The following fractions were obtained at 12-13 mm:

Fraction I,	b.p. 56-63°;	4.5 g
Fraction II,	b.p. 65-67°;	20.0 g (acetic ester);

d_4^{20} 0.8821; n_D^{20} 1.4259; found MR 49.95; calculated MR 50.03

The pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol was carried out in a 20 mm quartz tube filled with glass wool (50 g). The tube was placed in an electric furnace, and the pyrolysis was carried out at 430-450°, the acetic ester being supplied at the rate of 25 ml per hour. The pyrolyzate was collected in a receiver cooled with ice water; it was washed with water and 10-15% sodium carbonate solution to free it from acetic acid, and was dried over calcium chloride.

It was found that the pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol does not go at 250-350°; it goes only to a slight extent at 410-420°; and complete breakdown of the acetic ester into olefin and acetic acid occurs only at 430-450°.

Three fractionations of 7.5 g of the product yielded:

Fraction I,	b.p. 95-103°;	0.2 g
Fraction II,	b.p. 103-106°;	4.2 g (olefin)
Fraction III,	b.p. 110-120°;	1.5 g
Fraction IV,	b.p. 120-160°;	1.2 g
	Total	7.1 g

The main fraction was found to have b.p. 103.0-106.0°; d_4^{20} 0.7310; n_D^{20} 1.4158; found MR 38.38; calculated MR 38.67. The boiling point of 3,3,4-trimethyl-1-pentene is 105° [10], and that of 2,3,4-trimethyl--1-pentene is 106.7-107.7° [11].

In order to prove the structure of the olefin obtained, it was oxidized with 2% aqueous potassium permanganate. It was shown that the acid $C_7H_{14}O_2$ was present among the oxidation products. Titration with 0.1 N NaOH gave:

<div align="center">

Found K 305;

Calculated K 308,

</div>

K being the acid equivalent. The amide was prepared, $C_{17}H_{15}ONH_2$, m.p. 130-132°. The literature gives m.p. 133-134° for the amide $C_{17}H_{15}ONH_2$.

The ketone $C_7H_{14}O$ was isolated from the oxidation products; it had b.p. 128-130°; d_4^{20} 0.8054; n_D^{20} 1.4005; found MR 34.22; calculated MR 34.53. It gave a 2,4-dinitrophenylhydrazone, m.p. 93°.

<div align="center">

Found % N 19.02

$C_{13}H_{18}N_4O_4$. Calculated % N 19.07

</div>

According to Hickinbottom, in the hydrolysis of the acetic ester, only 3,3,4-trimethyl-1-pentene

$$CH_3 - CH - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH = CH_2$$
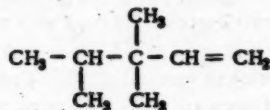
should be formed, and oxidation of this will give 2,2,3-trimethylbutyric and formic acids. However, oxidation with 2% aqueous potassium permanganate gave not only 2,2,3-trimethylbutyric acid, but also a ketone, b.p. 128-130°. The formation of the ketone $C_7H_{14}O$ indicates that in the pyrolysis of the acetic ester of 3,3,4--trimethyl-2-pentanol the resulting 3,3,4-trimethyl-1-pentene undergoes isomerization with formation of 2,3,4-trimethyl-1-pentene. Oxidation of the latter with 2% aqueous potassium permanganate gives formic acid and 3,4-dimethyl-2-pentanone:

$$CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - \underset{\underset{\displaystyle CH_3}{|}}{CH} - \underset{\underset{\displaystyle CH_3}{|}}{C} = CH_2 \xrightarrow{O_2} HCOOH + CH_3 - \underset{\underset{\displaystyle CH_3}{|}}{CH} - \underset{\underset{\displaystyle CH_3}{|}}{CH} - COCH_3$$
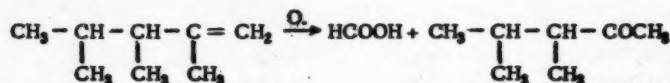
In order to establish the structure of the ketone obtained, 3,4-dimethyl-3-penten-2-one was synthesized from 2-methyl-2-butene by Kondakov's method [12], and this was then hydrogenated at room temperature over platinized charcoal (5% Pt). The boiling point of 3,4-dimethyl-2-pentanone was 133-135°, and it had d_4^{20} 0.8273; n_D^{20} 1.4087; found MR 34.10; calculated MR 34.53.

The 2,4-dinitrophenylhydrazone was prepared; it melted at 94-95°. A mixture of the 2,4-dinitrohydrazone of the ketone $C_7H_{14}O$ which we prepared by the oxidation of the olefin C_8H_{16} and the 2,4-dinitrophenylhydrazone of the ketone obtained in the confirmatory synthesis melted at 93-94°; i.e. there was no depression.

For comparison with the hydrocarbons obtained in the course of the transformations of 3,3,4-trimethyl--2-pentanol under the conditions of hydrogenational catalysis and also under the conditions of the pyrolysis of its acetic ester, 2,3,3-trimethylpentane was prepared by Grignard synthesis from 2-chloro-2,3-dimethyl-butane and ethylmagnesium bromide. 2-Chloro-2,3-dimethylbutane was prepared by shaking a mixture of 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene with twice its volume of hydrochloric acid (sp. gr. 1.19)

at room temperature for two hours. It had b.p. 108-110°; n_D^{20} 1.4168; d_4^{20} 0.8781; found MR 34.33; calculated MR 34.77.

The materials taken for the synthesis were 2-chloro-2,3-dimethylbutane (180 g), magnesium (36 g of turnings), ethyl chloride (96 g), and absolute ether (800 ml).

After decomposition of the reaction product and treatment by the usual methods, two fractionations yielded 2,3,3-trimethylpentane, b.p. 114-114.5°, in 28% yield. Traces of unsaturated hydrocarbons were removed from the 114-114.5° fraction by Tsvet's chromatographic adsorption method [14], which has been applied to the separation of hydrocarbons by Kazansky and Mikhailova, and the hydrocarbon was then again distilled over sodium. The following fractions were obtained:

Fraction I,	b.p. 102-114°;	1 ml
Fraction II,	b.p. 114-114.5°;	53 ml
Residue		5 ml
	Total	59 ml

The constants of the hydrocarbon were d_4^{20} 0.7275; n_D^{20} 1.4073; found MR 38.46; calculated MR 39.14.

Raman spectrum analysis showed that this hydrocarbon consisted only of 2,2,3-trimethylpentane.

SUMMARY

1. It was shown that, under the conditions of catalytic hydrogenation at 280-290° and 100-120 atm, 3,3,4-trimethyl-2-pentanol yields a mixture of 2,3,3- and 2,3,4-trimethylpentanes, the latter predominating. The formation of this mixture of isomers is due to the isomerization of the initial reaction product. 3,3,4-trimethyl-1-pentene.

2. It was shown that in the pyrolysis of the acetic ester of 3,3,4-trimethyl-2-pentanol at 430-450° isomerization again occurs, not only 3,3 4-trimethyl-1-pentene being formed, but also much 2,3,4-trimethyl-1-pentene [4]. This method for the preparation of hydrocarbons cannot therefore be recommended as a general method for the preparation of the higher branched olefins.

3. For comparison with the octane isomers obtained by the hydrogenation of 3,3,4-trimethyl-2-pentanol and by the pyrolysis of its acetic ester, 2,3,3-trimethylpentane was synthesized by the Grignard method.

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REACTIONS OF SYMMETRICAL AROMATIC MERCURY COMPOUNDS WITH PHENOLS

M.M. Koton and V.F. Martynova

Dimroth [1] was the first to show that the halides and acetate of mercury are able to mercurate aromatic hydrocarbons and their derivatives with formation of mono-, di-, and tri-mercurated compounds. The mercuration of phenols and amines proceeds particularly readily.

Koton and coworkers [2] showed that dialkyl and diaryl mercury compounds very readily mercurate phenols with formation of new organomercury compounds:

$$R_2Hg + R' C_6H_4OH \rightarrow RH + RHg C_6H_3 (OH) R'.$$
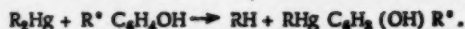
In the present investigation we have continued the study of this reaction: we have examined the behavior of diphenylmercury derivatives of general formula $(RC_6H_4)_2$ Hg with the object of determining the effect of the nature of the substituent R in the benzene ring of the organomercury compound on the rate and character of the reactions occurring with various phenols. For this purpose we took the following compounds:

1. Bis-p-aminophenylmercury $(p-H_2NC_6H_4)_2Hg$
2. Bis-o-hydroxyphenylmercury $(o-HOC_6H_4)_2Hg$
3. Bis-p-methoxyphenylmercury $(p-CH_3OC_6H_4)_2Hg$
4. Bis-m-nitrophenylmercury $(m-O_2NC_6H_4)_2Hg$
5. Bis-o-nitrophenylmercury $(o-O_2NC_6H_4)_2Hg$
6. Bis-p-carboxyphenylmercury $(p-HOOCC_6H_4)_2Hg$

The following phenols were used: pyrogallol, hydroquinone, resorcinol, phenol, p-cresol, p-aminophenol, p-nitrophenol, o-nitrophenol, m-nitrophenol, 2,4-dinitrophenol, 2,4,6-trinitrophenol, p-chlorophenol, 2,4-dichlorophenol, and 2,4,6-trichlorophenol.

Mercuration with symmetrical mercury compounds of formula $(RC_6H_4)_2$Hg requires the application of heat. On the basis of a radical mechanism for this reaction, it might be expected that the readiness with which mercuration occurs would depend on the thermal stability of the symmetrical mercury compound, low stability being associated with ready reaction with phenols.

A study was made of the thermal stability of symmetrical organomercury compounds at 130-150°. The experiments showed that the thermal stabilities of compounds of formula $(RC_6H_4)_2$Hg vary greatly. Organomercury compounds in which the substituent R in the benzene ring is COOH or NO_2, i.e. substituents of the "second kind", are thermally stable. Organomercury compounds in which R is NH_2, OH or OCH_3, i.e. substituents of the "first kind", decompose already at 130° with separation of mercury, the amount of mercury separating being dependent on the nature of the substituent in the benzene ring.

With respect to the extent of decomposition in three hours at 130°, these compounds can be arranged in the following series:

$$(p-H_2NC_6H_4)_2 Hg > (o-HOC_6H_4)_2 Hg > (p-CH_3OC_6H_4)_2 Hg$$

However, in our study of thermal decomposition we were unable to determine the difference in stability between compounds of formula $(RC_6H_4)_2$Hg having substituents of the "second kind" (i.e. NO_2 or COOH), because of their very high thermal stability (as shown in Table 1).

One of the present authors has shown [3] that polyhydric phenols (pyrogallol and others) accelerate the thermal decomposition of symmetrical mercury compounds, and we therefore studied the decomposition of $(RC_6H_4)_2$Hg in presence of pyrogallol at 130° and 150°. Under these conditions symmetrical mercury compounds having substituents of the "second kind" decomposed with separation of mercury (Table 2).

With respect to rate of decomposition these compounds form the series:

$$(m-NO_2C_6H_4)_2 Hg > (o-NO_2C_6H_4)_2 Hg > (p-HOOCC_6H_4)_2 Hg.$$
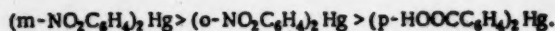
TABLE 1

Formula of compound	t°C	Time (hours)	Amount of mercury formed (%)	Analysis of residue for mercury	
				Found (%)	Calculated (%)
$(p-H_2NC_6H_4)_2Hg$	130	3	23.85	52.09	51.94
$(o-HOC_6H_4)_2Hg$	130	3	20.69	51.77	51.53
$(p-CH_3OC_6H_4)_2Hg$	130	3	5.05	47.90	48.30
$(m-NO_2C_6H_4)_2Hg$	150	3	None	45.20	45.04
$(o-NO_2C_6H_4)_2Ng$	150	3	None	44.97	45.04
$(p-HOOCC_6H_4)_2Hg$	160	3	None	44.98	44.82

TABLE 2

Formula of compound	t°C	Time (hours)	Amount of mercury formed (%)
$(p-H_2NC_6H_4)_2Hg$	130	3	86.85
$(p-CH_3OC_6H_4)_2Hg$	130	3	76.43
$(m-NO_2C_6H_4)_2Hg$	150	3	58.70
$(o-NO_2C_6H_4)_2Hg$	150	3	30.70
$(p-HOOCC_6H_4 Hg$	150	3	19.28

In order to determine the laws governing the strengths of bonds formed by radicals with mercury atoms in the symmetrical organo-mercury compounds studied, we investigated their decomposition in presence of monohydric phenols. It was found that, for the compounds containing substituents of the "first kind", the order of ease of decomposition was the same as for thermal decomposition (Table 3).

With respect to thermal stability, therefore, all of the compounds of general formula $(RC_6H_4)_2Hg$ that we have studied can be placed in the following order:

$$(p-H_2NC_6H_4)_2Hg < (o-HOC_6H_4)_2Hg < (p-CH_3OC_6H_4)_2Hg <$$
$$< (m-NO_2C_6H_4)_2Hg < (o-NO_2C_6H_4)_2Hg < (p-HOOCC_6H_4)_2Hg.$$
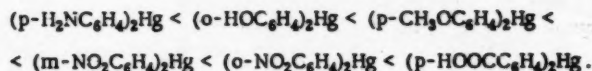
It was shown further that, in presence of the phenols pyrogallol, p-aminophenol, and hydroquinone, the organomercury compounds studied decompose with separation of mercury and without formation of mercurated compounds. This behavior could be explained in two ways: 1) by the high reducing power of these phenols; or 2) by the extremely low thermal stability of the mercurated derivatives of these phenols. It might be expected, therefore, that phenols of lower reducing power would be able to give stable mercurated derivatives with the symmetrical mercury compounds that we have chosen for investigation. It is in fact found that, when substituted phenols are heated with compounds of formula $(RC_6H_4)_2Hg$, they react with formation of new organomercury compounds.

The results obtained enable us to compare the thermal stabilities of the symmetrical mercury compounds with their reactivities in the mercuration reaction. The least thermally stable of these mercury compounds will mercurate phenols at the lowest temperatures (70-100°) with formation of mono-, di-, and tri-mercurated phenols. For example, when bis-p-aminophenylmercury is used, mono-, di-, and tri-mercurated phenols are formed already at 70° [4].

As the thermal stability of the compound $(RC_6H_4)_2Hg$ increases, its ability to give polymercurated compounds diminishes and more severe reaction conditions are required. For example, the reaction of bis-p--methoxyphenylmercury with phenols was carried out at 130-150°, and the main products were monomercurated derivatives of these phenols of general formula $p-CH_3OC_6H_4HgC_6H_3(OH)(R)$ [5]. When bis-o or bis-m--nitrophenylmercury was used, the reaction often did not go.

On the basis of our results it must be supposed that the mercuration of phenols by symmetrical mercury compounds passes through a stage in which the mercury compounds decompose into free radicals according to the equation:

$$RC_6H_4 - Hg - C_6H_4R \rightarrow RC_6H_4^\cdot + RC_6H_4Hg^\cdot.$$
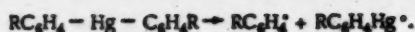
The radical $RC_6H_4^\cdot$, then reacts with a hydrogen of the benzene ring of the phenol with formation of the corresponding benzene derivative (aniline, anisole, or nitrobenzene). With respect to reactivity, the radicals formed can be arranged in the following order:

$$(p\text{-}H_2NC_6H_4)^\cdot > (o\text{-}HOC_6H_4)^\cdot > (p\text{-}CH_3OC_6H_4)^\cdot >$$

$$> (m\text{-}NO_2C_6H_4)^\cdot > (o\text{-}NO_2C_6H_4)^\cdot > (p\text{-}HOOCC_6H_4)^\cdot.$$
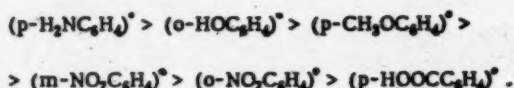
The sequence that we have found is fully in accord with those found previously by Kharasch, Nesmeyanov, Kocheshnikov, and Koton. It must be pointed out that we were the first to establish the position of the radical of o-nitrophenol in the Nesmeyanov-Kharasch series, and also to determine the relative positions of the o- and m-nitrophenyl radicals. The study of the reactions between symmetrical organomercury compounds and phenols has enabled us to determine some of the laws governing the behavior of substituted phenols. As shown previously, reaction of symmetrical organomercury compounds with phenols results in the formation, on the one hand, of mercurated phenols, and on the other, of metallic mercury. We estimated the reactivities of the phenols on the basis of the amount of mercury that separated in the course of the mercuration reaction; the results were compared with those for unsubstituted phenol.

TABLE 3

Formula of compound	t°C	Amount of mercury formed (%) in reaction with	
		p-amino-phenol	hydroquinone
$(p\text{-}H_2NC_6H_4)_2Hg$	130	74.50	72.38
$(p\text{-}CH_3OC_6H_4)_2Hg$	130	58.26	52.20
$(m\text{-}NO_2C_6H_4)_2Hg$	150	19.75	9.50
$(o\text{-}NO_2C_6H_4)_2Hg$	150	8.79	8.21

The phenols that we studied can be divided into two groups. The first of these consists of phenols that do not form stable mercurated derivatives; when they are treated with compounds of the type $(RC_6H_4)_2Hg$, only the separation of metallic mercury is observed. The phenols of this group include pyrogallol, p-aminophenol, and hydroquinone. The second group consists of phenols which, when treated with compounds of the type $(RC_6H_4)_2Hg$, give the corresponding mercurated compounds, as well as a little metallic mercury. This group includes phenol, p-cresol, resorcinol, p-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, p-, o-, and m-nitrophenols, 2,4-dinitrophenol, and 2,4,6-trinitrophenol. In their turn, phenols of the second group can be divided into two groups according to the nature of the substituents: 1) phenols having substituents of the "first kind", and 2) phenols having substituents of the "second kind".

When they react with organomercury compounds of the type $(RC_6H_4)_2Hg$, phenols having substituents of the "first kind" yield more metallic mercury than phenols having substituents of the "second kind", with the exception of 2,4,6-trichlorophenol, which behaves like the nitrophenols (Table 4).

The results of our investigations of the reaction of phenols with symmetrical organomercury compounds of the type $(RC_6H_4)_2Hg$ permit us to make the following general statements:

1) Increase in the number of hydroxyl groups in the benzene ring of phenols results in increase in reactivity.

These phenols form the series:

2) Introduction of chlorine atoms into the benzene ring of phenol increases the reactivity, an exception being 2,4,6-trichlorophenol, which is less reactive probably owing to a steric-hindrance effect. The behavior of chlorophenols in reactions with $(RC_6H_4)_2Hg$ can be represented by the following series:

3) Introduction of a nitro group into the benzene ring of phenol lowers the reactivity (with the exception of m-nitrophenol, which is highly reactive). With respect to the extent to which mercury separates in their reactions with organomercury compounds of the type $(RC_6H_4)_2Hg$, nitrophenols may be arranged in the series:
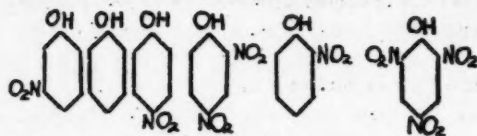
4) It must be noted that the amount of mercury that separates in the reaction of $(RC_6H_4)_2Hg$ with phenols depends both on the nature of the phenol and on the nature of the organomercury compound. Thus, the phenols p-cresol, p-chlorophenol, and hydroquinone in their reactions with bis-p-aminophenylmercury and bis-p-methoxyphenylmercury may be placed in the following order with respect to the amount of mercury that separates:
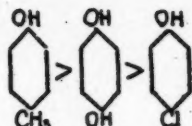
When the reaction is carried out with bis-m- or bis-o-nitrophenylmercury, the sequence of the phenols is reversed:
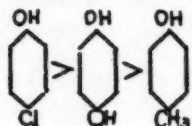
The results obtained indicate that the separation of mercury during the mercuration of phenols proceeds through the stage of the formation of mercurated phenols, which are then decomposed; i.e. it is not an independent reaction occurring at the same time as mercuration. The stability of the mercurated phenol will depend not only on the structure of the phenol residue, but also on the nature of the organic radical attached to the mercury atom of the mercurated phenol.

EXPERIMENTAL

In all experiments a mixture of the substances was heated in sealed tubes in thermostats regulated at 50°, 70°, 100°, 130°, and 150° for periods ranging from 1 to 12 hours; 0.5-0.6 g of reactants was taken. When the tubes were opened, it was always found that the corresponding benzene derivative (aniline, anisole, nitrobenzene) was floating on the reaction mixture. This substance was removed and with the object of isolating the solid reaction products. the reaction mixture was extracted successively with various solvents (ether, alcohol, benzene, chloroform). The monomercurated compounds were generally readily soluble in one of these solvents. and they were obtained in the pure state by recrystallization. Di- and tri-mercurated compounds are insoluble in organic solvents and they were purified by dissolution in 0.5 N caustic alkali and reprecipitation with carbon dioxide. The structures of some of the mercurated phenols were proved by cleavage with bromine or iodine, when the organomercury radical was replaced by a halogen atom. The resulting bromo- or iodo-phenol was identified by its melting point and by a mixture melting point test.

Mercury was determined volumetrically in the mercurated products. The 44 new mono-, di-, and tri--mercurated phenols listed in Table 5 were prepared and characterized.

TABLE 4

$(RC_6H_4)_2Hg$	Phenol	t°C	Time (hours)	Amount of metallic mercury (%)
$(p-H_2NC_6H_4)_2Hg$	Pyrogallol	130	3	86.86
$(p-H_2NC_6H_4)_2Hg$	Hydroquinone	130	3	72.38
$(p-H_2NC_6H_4)_2Hg$	Phenol	130	3	49.50
$(p-CH_3OC_6H_4)_2Hg$	Pyrogallol	130	3	76.43
$(p-CH_3OC_6H_4)_2Hg$	Hydroquinone	130	3	52.20
$(p-CH_3OC_6H_4)_2Hg$	Phenol	130	3	5.63
$(p-H_2NC_6H_4)_2Hg$	o-Chlorophenol	150	3	83.71
$(p-H_2NC_6H_4)_2Hg$	p-Chlorophenol	150	3	80.49
$(p-H_2NC_6H_4)_2Hg$	Phenol	150	3	68.25
$(p-H_2NC_6H_4)_2Hg$	Trichlo.ophenol	150	3	58.00
$(p-H_2NC_6H_4)_2Hg$	m-Nitrophenol	150	3	80.87
$(p-H_2NC_6H_4)_2Hg$	p-Nitrophenol	150	3	60.04
$(p-H_2NC_6H_4)_2Hg$	2,4-Dinitrophenol	150	3	53.79
$(p-H_2NC_6H_4)_2Hg$	o-Nitrophenol	150	3	10.02
$(p-H_2NC_6H_4)_2Hg$	Trinitrophenol	150	3	6.00
$(m-O_2NC_6H_4)_2Hg$	Pyrogallol	150	3	68.70
$(m-O_2NC_6H_4)_2Hg$	Hydroquinone	150	3	9.60
$(m-O_2NC_6H_4)_2Hg$	Phenol	150	3	3.56
$(o-O_2NC_6H_4)_2Hg$	Pyrogallol	150	3	30.70
$(o-O_2NC_6H_4)_2Hg$	Hydroquinone	150	3	8.70
$(o-O_2NC_6H_4)_2Hg$	Phenol	150	3	0.00

TABLE 5

No.	Formula of compound	M.p. (°C)	Appearance of crystals	Solubility in organic solvents
1	2	3	4	5
1	$(p-H_2NC_6H_4Hg)_2C_6H_2(OH)(NO_2)$	Does not melt below 280°	Dark blue	Insoluble
2	$(p-H_2NC_6H_4Hg)_2C_6H_2(OH)(NO_2)$	Does not melt below 260°	Orange	Ditto
3	$(p-H_2NC_6H_4Hg)C_6H_2(OH)(NO_2)_2$	203-205	*	In benzene
4	$(p-H_2NC_6H_4Hg)C_6H(OH)(NO_2)_3$	192-195	*	In chloroform
5	$(p-H_2NC_6H_4Hg)C_6H_3(OH)(Cl)$	180-181	Yellow	In alcohol
6	$(p-H_2NC_6H_4·$ $_6)_3C_6H(OH)(Cl)$	Does not melt below 260°	Dark green	Insoluble
7	$(p-H_2NC_6H_4Hg)_2C_6H(OH)(Cl)_2$	Does not melt below 260°	Dark red	Ditto
8	$(p-H_2NC_6H_4Hg)_2C_6H(OH)(Cl)_2$	195-197	Green	In alcohol and ether
9	$(p-H_2NC_6H_4Hg)_2C_6(OH)(Cl)_3$	Does not melt below 260°	Dark blue	Insoluble
10	$(p-H_2NC_6H_4Hg)_2C_6H_2(OH)_2$	Decomposes at 200°	Light green	Sparingly soluble in alcohol
11	$(p-H_2NC_6H_4Hg)_3C_6H(NO_2)_2$	Does not melt below 260°	Dark green	Insoluble
12	$(p-H_2NC_6H_4Hg)_3C_6H_2(OH)$	179	White	In alcohol and chloroform
13	$(p-H_2NC_6H_4Hg)_3C_6H(OH)CH_3$	Does not melt below 260°	Fine white	Insoluble
14	$(p-CH_3OC_6H_4Hg)_2C_6H_2(OH)(NO_2)$	Ditto	Yellow	Ditto

TABLE 5 (continued)

1	2	3	4	5
15	$(p\text{-}CH_3OC_6H_4Hg)C_6H_3(OH)(NO_2)$	109-110	Orange	In benzene
16	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)(NO_2)$	Does not melt below 260°	Yellow	Insoluble
17	$(p\text{-}CH_3OC_6H_4Hg)C_6H_2(OH)(NO_2)_2$	127-129	"	In chloroform
18	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H(OH)(NO_2)_2$	Does not melt below 260°	Orange	Insoluble
19	$(p\text{-}CH_3OC_6H_4Hg)C_6H(OH)(NO_2)_3$	125-126	Yellow	In alcohol and chloroform
20	$(p\text{-}CH_3OC_6H_4Hg)C_6H_3(OH)(Cl)$	154-156	White	In chloroform
21	$(p\text{-}CH_3OC_5H_4Hg)_2C_6H_2(OH)(Cl)$	Does not melt below 260°	"	Insoluble
22	$(p\text{-}CH_3OC_6H_4Hg)C_6H_2(OH)(Cl)_2$	Decomposes at 200°	Fine white	In alcohol
23	$(p\text{-}CH_3OC_6H_4Hg)C_6H(OH)(Cl)_3$	179-181	White	In benzene
24	$(p\text{-}CH_3OC_6H_4Hg)_2C_6(OH)(Cl)_3$	Does not melt below 260°	"	Insoluble
25	$(p\text{-}CH_3OC_6H_4Hg)C_6H_3(OH)_3$	169-171	Orange	In chloroform
26	$(p\text{-}CH_3OC_6H_4Hg)_3C_6H(OH)_2$	Does not melt	Fine yellow	Insoluble
27	$(p\text{-}CH_3OC_6H_4Hg)_2C_6H_2(OH)(CH_3)$	Does not melt below 250°	White regular prisms	In chloroform
28	$(p\text{-}CH_3OC_6H_4Hg)_3C_6H_2(OH)$	208	Large white prisms	In benzene
29	$(m\text{-}NO_2C_6H_4Hg)C_6H_3(OH)(NO_2)$	238-240	Orange	In pyridine
30	$(m\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(NO_2)_2$	253-254	Yellow	In benzene
31	$(m\text{-}NO_2C_6H_4Hg)C_6H(OH)(NO_2)_3$	Does not melt below 250°	Pink	Insoluble
32	$(m\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(Cl)_2$	151-153	Dark red	In chloroform
33	$(m\text{-}NO_2C_6H_4Hg)C_6H(OH)(Cl)_3$	Does not melt below 260°	Pink	Insoluble
34	$(m\text{-}NO_2C_6H_4Hg)_2C_6H_2(OH)_2$	Does not melt below 260°	Yellow	Ditto
35	$(m\text{-}NO_2C_6H_4Hg)C_6H_3(OH)(Cl)_3$	Does not melt below 250°	Dark yellow	Insoluble
36	$(o\text{-}NO_2C_6H_4Hg)C_6H_3(OH)(NO_2)$	187-188	Fine yellow	In benzene
37	$(o\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(NO_2)_2$	196-197	Light yellow	In benzene and petroleum ether
38	$(o\text{-}NO_2C_6H_4Hg)C_6H(OH)(NO_2)_3$	181-183	Yellow	In petroleum ether
39	$(o\text{-}NO_2C_6H_4Hg)_2C_6H_2(OH)(Cl)$	Does not melt below 260°	Brown	Insoluble
40	$(o\text{-}NO_2C_6H_4Hg)C_6H_2(OH)(Cl)_2$	148	White	In benzene
41	$(o\text{-}NO_2C_6H_4Hg)C_6H(OH)(Cl)_3$	210-211	"	Ditto
42	$(o\text{-}NO_2C_6H_4Hg)_2C_6H_2(OH)_2$	Does not melt below 250°	Pink	Insoluble
43	$(o\text{-}NO_2C_6H_4Hg)C_6H_3(OH)(CH_3)$	185	Yellow	In ether
44	$(m\text{-}NO_2C_6H_4Hg)_2C_6H_2(OH)(Cl)$	Does not melt below 260°	Pink	Insoluble

SUMMARY

1. It was shown that diaryl mercury compounds of general formula $(RC_6H_4)_2Hg$ ($R = NH_2$, NO_2, OCH_3, and OH) are able to mercurate phenols at 70-150° with formation of mono-, di-, and tri-mercurated compounds.

2. The rate of mercuration and the composition of the products vary with the nature of the substituents present in the organomercury compound and in the phenol.

3. With respect to reactivity the compounds $(RC_6H_4)_2Hg$ can be arranged in the series:

$$(p-H_2NC_6H_4)_2Hg > (o-HOC_6H_4)_2Hg > (p-CH_3OC_6H_4)_2Hg > (m-NO_2C_6H_4)_2Hg >$$

$$> (o-NO_2C_6H_4)_2Hg > (p-HOOCC_6H_4)_2Hg$$
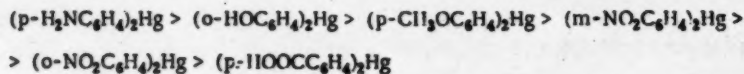
4. Phenols having substituents of the "first kind" (p-cresol, resorcinol, chlorophenols) are mercurated more readily than phenols having substituents of the "second kind" (nitrophenols).

5. A free-radical mechanism is proposed for the mercuration of phenols by mercury compounds of formula $(RC_6H_4)_2Hg$.

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•T.p. = C.B. Translation pagination

ABSORPTION SPECTRA AND MOLECULAR STRUCTURE

COMMUNICATION 5. SPECTROSCOPIC INVESTIGATIONS OF SOLUTIONS OF CHLORINE-SUBSTITUTED PHENYLHYDRAZONES OF 9-ACRIDINECARBOXALDEHYDE HYDROCHLORIDE IN ALCOHOLIC HYDROGEN CHLORIDE •

A.A. Kharkharov

We have shown previously that as the degree of substitution of chlorine derivatives of aniline is increased the position of the principal absorption maximum, measured in alcoholic solution, is displaced in the direction of the longer waves. We found also that departures from additivity in the effects of the substituents were comparatively small for chlorine, the extent of the discrepancy being dependent on the number and positions of the substituents [1]. These conclusions have now been shown to be valid for the ultraviolet and visible spectra of solutions of chlorine-substituted phenylhydrazones of 9-acridinecarboxaldehyde hydrochloride in alcoholic hydrogen chloride:
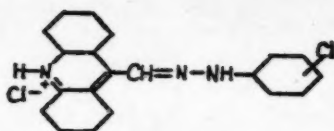
The introduction of chlorine and other electron-accepting substituents [2] into the molecule of this compound is accompanied not by deepening of color, as was found for aniline, but by lightening. With respect to the hypsochromic effect of the halogen, monochloro derivatives fall into the order (Fig. 1, Table 1) corresponding to the demands of the inductive effect of the substituent [3]:

<p align="center">ortho > meta > para</p>

In the present investigation we have found a regular displacement of the principal absorption maximum in the direction of the shorter waves as the number of substituents increase, the sequence being as follows:
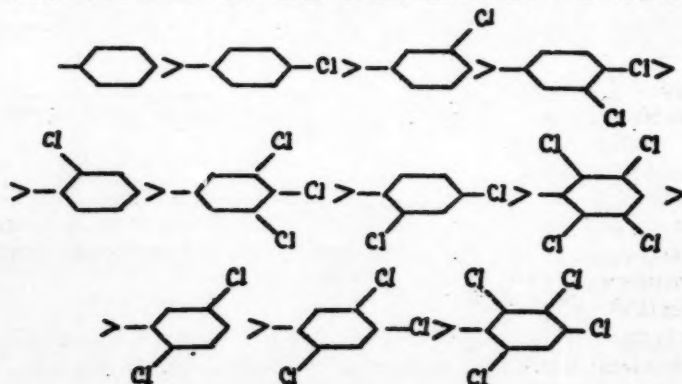
Again, precise additivity in the effect of substituents on the position of the principal absorption band was scarcely ever observed, and our attention is drawn once more to the profound significance of the Butlerov-Markovnikov dialectical thesis relating to the mutual effects of atoms and of groups of atoms.

• Work carried out in fulfilment of requirements for the doctorate of the Institute of Organic Chemistry of the USSR Academy of Sciences.

The spectrum investigations were carried out over the range 210-700 mµ with an SF-1 photoelectric spectrophotometer. The solvent used was 0.2 N alcoholic HCl, and effects due to solvent were excluded. The measurements were made on dye solutions of identical concentration. All of the substances were prepared under the conditions that we have used previously for the preparation of 9-acridinecarboxaldehyde phenylhydrazone [4-6]. Their purities were checked by combustion analysis for nitrogen (Table 1).

Fig. 1. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde p-chlorophenyl-hydrazone; 2 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 3 - 9-acridine-carboxaldehyde o-chlorophenylhydrazone
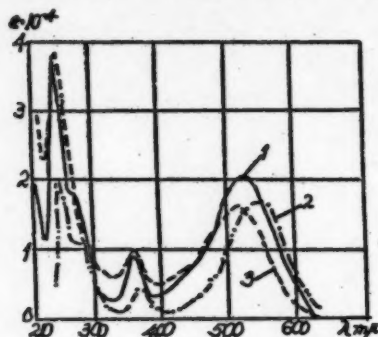
Fig. 2. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde o-chlorophenyl-hydrazone; 2 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 3 - 9-acridine-carboxaldehyde 2,5-dichlorophenylhydrazone

The principal absorption band of the 2,4-isomer has the lowest intensity, and that of the 2,5-isomer has the shortest wavelength ($\Delta\lambda = -52$ mµ). The isomer in which there

The principal absorption maxima of the o-, m-, and p-chlorophenylhydrazones of 9-acridine-carboxaldehyde lie at 533, 548, and 554 mµ, respectively.

Of the three dichloro derivatives that we examined, the 2,5-isomer showed the greatest departure from additivity (-9 mµ, Table 1, Fig. 2). For the 2,4-isomer, the departure from the calculated value of the displacement of the principal absorption maximum is only 2mµ (Table 1, Fig. 3). For the 3,4-isomer, the experimentally found and calculated values of the wavelength at the principal absorption maximum coincide (Table 1, Fig. 4). The introduction of two halogen atoms into the molecule of 9-acridinecarboxaldehyde phenylhydrazone hydrochloride has little effect on the form of the curve (Fig. 5). The relative intensities of the absorption bands— $\epsilon_1 > \epsilon_3 > \epsilon_2$ — are maintained. The intensity of the principal maximum is reduced.

Fig. 3. Absorption spectra in alcoholic HCl: 1 - 9-acridinecarboxaldehyde p-chlorophenylhydra-zone; 2 - 9-acridinecarboxaldehyde o-chlorophenyl-hydrazone; 3 - 9-acridinecarboxaldehyde 2,4-di-chlorophenylhydrazone

is no ortho chlorine absorbs at the longest waves (Table 1, Fig. 5). The short-wave absorption bands of the dichloro derivatives are almost identical. All that we have written about the dichloro derivatives of the phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride can be applied also to the trichloro derivatives (Table 1, Fig. 6). Introduction of the three halogen atoms in the 2,4,5-positions displaces the principal maximum to a greater extent ($\Delta\lambda = -52$ mµ, Table 1, Fig. 6) than their introduction into the 3,4,5-positions ($\Delta\lambda = -37$ mµ, Table 1, Fig. 7). For both isomers the departure from additivity is very slight - only - 1 mµ Table 1, Fig. 6).

•See footnote on page 988 before the summary.

TABLE 1

Additivity of the Effects of Chlorine Atoms in Chlorine-substituted Phenylhydrazones of 9-Acridinecarboxaldehyde Hydrochloride
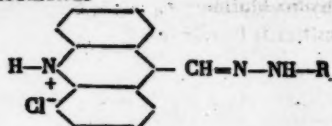
on the Position of the Principal Maximum. Results for Analysis for Nitrogen

R	Principal absorption maximum (mμ)	Displacement of maximum Observed (mμ)	Displacement of maximum Calculated (mμ)	Departure from additivity (mμ)	Molecular formula	Nitrogen content (%) Found	Nitrogen content (%) Calculated
(phenyl)	562	0	—	—	$C_{20}H_{12}N_3$	14.4	14.1
(2-Cl)	533	−29	—	—	$C_{20}H_{14}N_3Cl$	12.8	12.7
(3-Cl)	548	−14	—	—	$C_{20}H_{14}N_3Cl$	12.6	12.7
(4-Cl)	554	− 8	—	—	$C_{23}H_{24}N_2Cl$	12.0	12.7
(2,3-Cl)	523	−39	−37	− 2	$C_{20}H_{13}N_3Cl_2$	11.9	11.5
(2,5-Cl)	510	−52	−43	− 9	$C_{20}H_{13}N_3Cl_2$	11.8	11.5
(3,4-Cl)	540	−22	−22	0	$C_{20}H_{13}N_3Cl_2$	11.9	11.5
(2,4,5-Cl)	510	−52	−51	− 1	$C_{20}H_{12}N_3Cl_3$	10.8	10.5
(2,3,4-Cl)	525	−37	−36	− 1	$C_{20}H_{12}N_3Cl_3$	10.7	10.5
(2,3,4,6-Cl)	509	−53	−80	+27	$C_{20}H_{11}N_3Cl_4$	9.8	9.6
(2,3,5,6-Cl)	512	−50	−86	+36	$C_{23}H_{11}N_5Cl_4$	9.8	9.6

When the number of halogen atoms in the molecule is increased further, a considerable departure from additivity occurs — a transition from a quantitative to a qualitative effect. For the 2,3,4,6-tetrachloro derivative the departure from additivity is + 27 mμ (Table 1, Fig. 9). It is probable that it is at this

point that a great disturbance of the planar configuration of the molecule occurs. Increase in the number of halogen atoms is accompanied by a great change in the intensity of the principal absorption band. The sequence of intensities of the absorption bands characteristic for the unsubstituted phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride— $\epsilon_1 > \epsilon_3 > \epsilon_2$ — breaks down for the tetrahalo derivatives; a different sequence of intensities is found— $\epsilon_1 > \epsilon_2 > \epsilon_3$ (Figures 8 and 9).
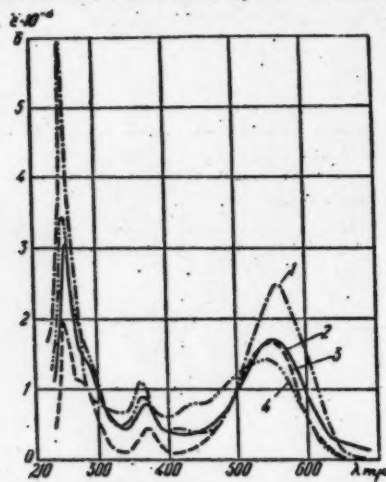
Fig. 4. Absorption spectra in alcoholic HCl:
1 - 9-acridinecarboxaldehyde 3,4-dichlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde p-chlorophenylhydrazone; 4 - 9-acridinecarboxaldehyde phenylhydrazone.
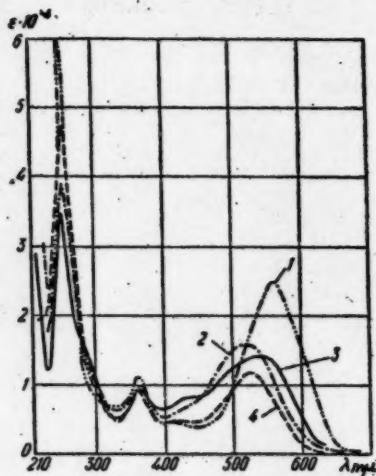
Fig. 5. Absorption spectra in alcoholic HCl:
1 - 9-acridinecarboxaldehyde 3,4-dichlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde 2,4-dichlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde 2,5-dichlorophenylhydrazone; 4 - 9-acridinecarboxaldehyde phenylhydrazone.
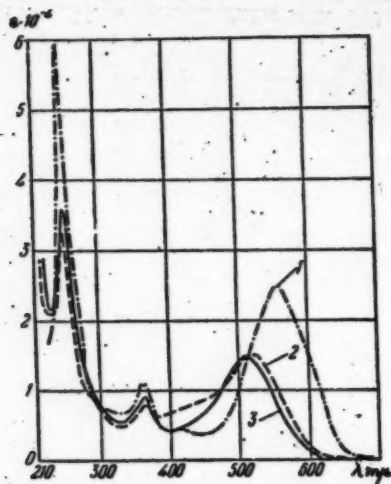
Fig. 6. Absorption spectra in alcoholic HCl:
1 - 9-acridinecarboxaldehyde 2,4,5-trichlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde 3,4,5-trichlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde phenylhydrazone.
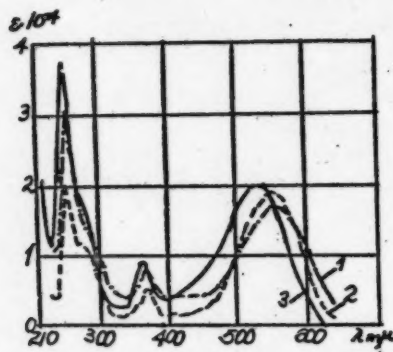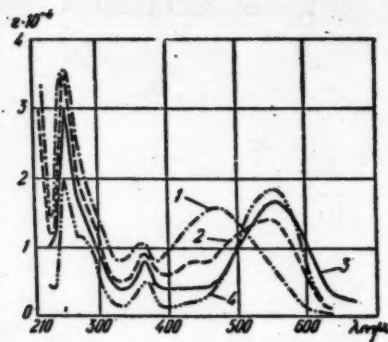

Fig. 7. Absorption spectra in alcoholic HCl:
1 - 9-acridinecarboxaldehyde 3,4,5-trichlorophenylhydrazone; 2 - 9-acridinecarboxaldehyde 3,4-dichlorophenylhydrazone; 3 - 9-acridinecarboxaldehyde m-chlorophenylhydrazone; 4 - 9-acridinecarboxaldehyde p-chlorophenylhydrazone.

TABLE 2

Principal Properties of New Chloro Derivatives of the Phenylhydrazone of 9-Acridinecarboxaldehyde Hydrochloride

No.	Name of Compound	M.p. (°C)	Color of dry substance		Color of solution					Principal absorption maximum mμ		
			In free state	as salt with acid	in aqueous alcoholic caustic soda	in alcohol	in alcoholic caustic soda	in concentrated sulfuric acid	in glacial acetic acid	in alcohol	in 0.2 N alcoholic HCl	in glacial acetic acid
1	9-Acridinecarboxaldehyde o-chlorophenylhydrazone	210	y	r-black	y	y	y-g	y	r-v	440	533	530
2	9-Acridinecarboxaldehyde m-chlorophenylhydrazone	218	y	v-black	o	o	y-g	y	r-v	450	548	550
3	9-Acridinecarboxaldehyde 2,4-dichlorophenylhydrazone	175	y	black	y	y	g	g-x	r	437	523	525
4	9-Acridinecarboxaldehyde 2,5-dichlorophenylhydrazone	210	y-br	g-black	y	y	g-br	g-br	r	430	510	510
5	9-Acridinecarboxaldehyde 3,4-dichlorophenylhydrazone	192	y-br	g-black	y	y	g-br	g-br	r	445	540	540
6	9-Acridinecarboxaldehyde 2,4,5-trichlorophenylhydrazone	172	br	g-black	y	y	–	br	r	–	510	510
7	9-Acridinecarboxaldehyde 3,4,5-trichlorophenylhydrazone	238	y-br	r-black	y	y	blue	y-g	r	440	525	525
8	9-Acridinecarboxaldehyde 2,3,4,6-tetrachlorophenylhydrazone	142	br	–	y	y	br	g-br	r	–	509	510
9	9-Acridinecarboxaldehyde 2,3,5,6-tetrachlorophenylhydrazone	155	br	–	y	y	o	br	r	–	512	510

Abbreviations: y – yellow; g – green; r – red; br – brown; o – orange; v – violet
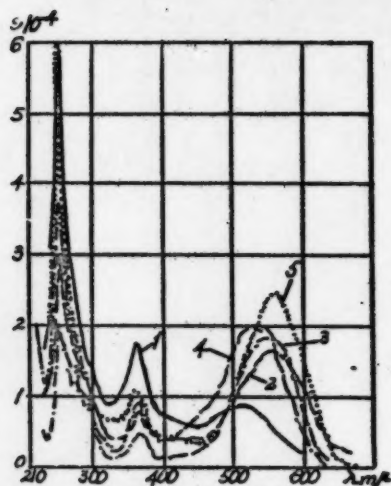
Fig. 8. Absorption spectra in alcoholic HCl:
1 - 9-acridinecarboxaldehyde 2,3,4,6-tetra-
chlorophenylhydrazone; 2 - 9-acridinecar-
boxaldehyde p-chlorophenylhydrazone; 3 -
9-acridinecarboxaldehyde m-chlorophenyl-
hydrazone; 4 - 9-acridinecarboxaldehyde
o-chlorophenylhydrazone; 5 - 9-acridine-
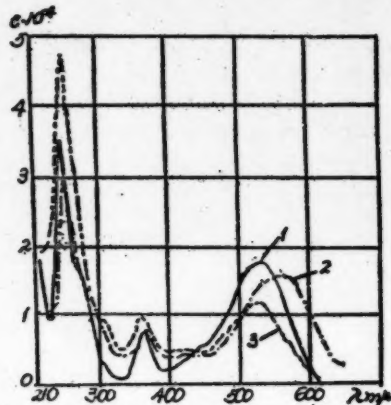carbonaldehyde phenylhydrazone
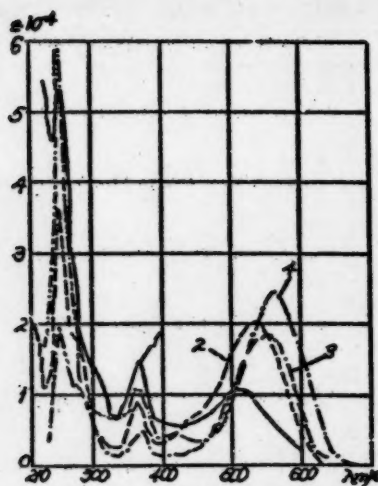
Fig. 9. Absorption spectra in alcoholic HCl; 1 - 9-
acridinecarboxaldehyde 2,3,5,6-tetrachlorophenyl-
hydrazone; 2 - 9-acridinecarboxaldehyde o-chloro-
phenylhydrazone; 3 - 9-acridinecarboxaldehyde
m-chlorophenylhydrazone; 4 - 9-acridinecarboxal-
dehyde phenylhydrazone.

Comparison of the positions of the principal absorption maxima of the isomeric tetrachloro derivatives shows that four halogen atoms in the 2,3,4,6-positions have a more powerful hypsochromic effect ($\Delta\lambda =$ $= -53$ mμ, Table 1) than four halogens in the 2,3,5,6-positions ($\Delta\lambda = -50$ mμ, Table 1). Analogous regularities are observed for bromo, iodo, sulfo, nitro, carboxy, methyl, methoxy, and other derivatives of the phenylhydrazone of 9-acridinecarboxaldehyde hydrochloride.

The principal properties of the new chloro derivatives of the phenylhydrazone of 9-acridinecarboxalde-hyde hydrochloride are given together with results of analysis for nitrogen in Tables 1 and 2.

*There are discrepancies between the absorption graphs and the information given in Table 1 and the text. For example, it would appear that the curves labeled 1 in Figures 4, 5, and 6 all refer to unsubstituted 9-acridine-carboxaldehyde phenylhydrazone and not to the various substances indicated below the graphs. No attempt has been made to correct the labeling. - Publisher.

SUMMARY

1. The absorption spectra of solutions of mono-, di-, tri-, and tetra-chloro derivatives of the phenyl-hydrazone of 9-acridinecarboxaldehyde hydrochloride in alcoholic hydrogen chloride were investigated.

2. It was shown that, with respect to the hypsochromic effects of their halogen atoms, the monochloro derivatives fall into the sequence corresponding to the demands of the inductive effect of the substituent.

3. The presence of the substituents has little effect on the general shape of the curve and the positions of the short-wave absorption maxima. As the number of substituents increases, there is a regular displacement of the principal absorption maximum in the direction of the short waves. The effects of the substituents are approximately additive.

4. It can be inferred from the behavior of the chlorine derivatives of the phenylhydrazone of 9-acridine-carboxaldehyde hydrochloride that complete additivity of the effects of substituents is practically never observed. This fact is to be attributed to the mutual effects of atoms.

5. Nine new chloro derivatives of 9-acridinecarboxaldehyde phenylhydrazone were prepared.

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COMPARATIVE STUDY OF THE OXIDATION REACTIONS OF PECTIC SUBSTANCES, OF CELLULOSE, AND OF THE STRUCTURAL UNITS OF THESE SUBSTANCES

COMMUNICATION 3. COMPARATIVE STUDY OF THE REACTIVITIES OF THE STRUCTURAL UNITS CF CELLULOSE AND PECTIC SUBSTANCES IN OXIDATION REACTIONS WITH SODIUM METAPERIODATE AND HYDROGEN PEROXIDE

O. P. Golova and N. S. Mayat

We have shown that pectic substances present in the cotton fiber retard the oxidative degradation of cellulose which occurs when the fiber is treated with oxidizing agents in an alkaline medium. The results that we obtained can be regarded as a proof of the great tendency, relative to that of cellulose, of pectic substances to undergo oxidative degradation when these polymers occur in intimate association with the cotton fiber. This proof is a purely qualitative one and can give only a qualitative answer to the question of the relative rates at which cellulose and pectic substances present in the cotton fiber are oxidized.

It may be supposed that the difference in rate of oxidation between cellulose and pectic substances is to be attributed not only to differences in physical structure, but also to differences in chemical structure. The effect of chemical structure can be established only by a comparison of the rates of oxidation of the elementary structural units of cellulose and pectic substances, the effect of the structures of the polymers on their rates of oxidation being completely excluded. Such an investigation could be made only as the result of a comparative study of the reactivities of models of the elementary structural units of cellulose and polygalacturonic acid.

The structural unit of polygalacturonic acid differs from that of cellulose in that C-6 forms part of a carboxyl group and the hydrogen and hydroxyl at C-4 have the opposite spatial arrangement:
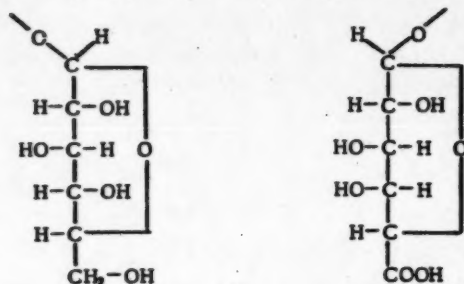
It may be supposed that this difference in structure between the structural units of cellulose and polygalacturonic acid will give rise to differences in reactivity and, therefore, in rates of oxidation. As approximate models of the structural units of these polymers we took methyl a-glucoside and methyl a-galactosiduronic acid, which, like the actual structural units, differ in the configuration at C-4 and in the identity of the functional group at C-6. Any difference, therefore, in the reactivities of these models can be ascribed to two causes: diastereoisomerism and the presence of a carboxyl in the one where the other has a primary alcohol group.

We made separate investigations of the effects of these two factors by making comparisons of reactivity for two pairs of model substances. We studied the effect of the first factor — diastereoisomerism — by comparing the reactivities of diastereoisomers differing only in the configuration at C-4 (methyl a-glucoside and methyl a-galactoside); and we studied the effect of the second factor — the presence of a carboxyl instead of a primary alcohol group — by comparing substances having the same configurations at all
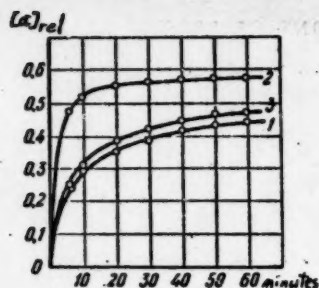
Fig. 1. Oxidation by sodium metaperiodate (2 moles per mole of carbohydrate) in an acid medium at 25°: 1) methyl a-glucoside; 2) methyl a-galactoside; 3) methyl a-galactosiduronic acid (concentration 2.5%).
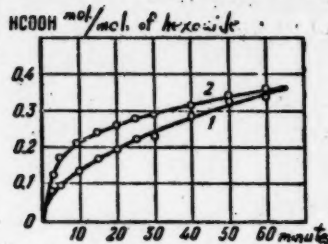
Fig. 2. Oxidation by sodium metaperiodate (2 moles per mole of carbohydrate) in an acid medium: 1) methyl a-glucoside; 2) methyl a-galactoside (concentration 0.25%).
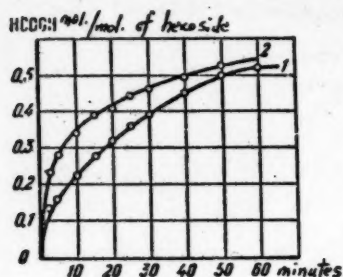
Fig. 3. Oxidation by sodium metaperiodate (4 moles per mole of carbohydrate) in an acid medium: 1) methyl a-glucoside; 2) methyl a-galactoside (concentration 0.25%).
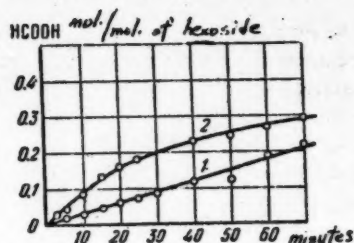
Fig. 4. Oxidation by sodium metaperiodate (4 moles per mole of carbohydrate) in an acid medium: 1) methyl a-glucoside; 2) methyl a-galactoside (concentration 0.125%).
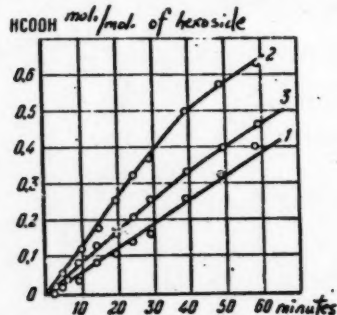
Fig. 5. Oxidation by sodium metaperiodate (4 moles per mole of carbohydrate) in an alkaline medium: 1) methyl a-glucoside; 2) methyl a-galactoside; 3) methyl a-galactosiduronic acid (concentration 0.125%).
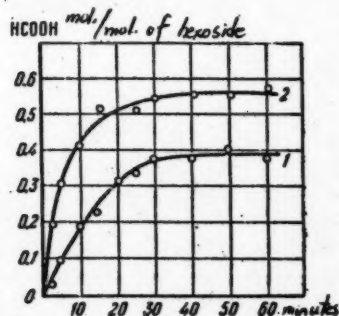
Fig. 6. Oxidation by hydrogen peroxide (4 moles per mole of carbohydrate) in an alkaline medium: 1) methyl a-glucoside; 2) methyl a-galactoside (concentration 0.25%).

Fig. 7. Oxidation by hydrogen peroxide (4 moles per mole of carbohydrate) in an alkaline medium: 1) methyl a-glucoside; 2) methyl a-galactoside; 3) methyl a-galactosiduronic acid (concentration 0.25%).

asymetric carbon atoms but different functional groups at C-6 (methyl a-galactoside and methyl a-galactosiduronic acid).

The reactivities of these hexosides were studied in oxidation reactions with sodium metaperiodate and hydrogen peroxide under the conditions that we have used previously in a study of the degradation of pectic substances [1] (oxidation with $NaIO_4$ at 20°, and with H_2O_2 at 92°). The amount of oxidant taken for reaction was that required theoretically for complete rupture of the pyran ring, i.e. two moles of oxidant per mole of carbohydrate. In some experiments 100% excess was taken.

For the investigation of the relative reactivities of these hexosides, two methods were used: 1) polarimetry, and 2) quantitative determination of formic acid. The application of polarimetry for this purpose was possible because oxidation of these hexosides by sodium metaperiodate yields oxidation products that are of one type, or even identical, and cause the specific rotation to change in the same direction (a reduction). The reactivities of these hexosides can therefore be characterized by the relative changes in specific rotation occurring during the oxidation process.

The use of the determination of formic acid for this purpose is based on the fact that in the oxidation of these hexosides by sodium metaperiodate, one mole of hexoside gives one mole, quantitatively, of formic acid [2]. Under certain conditions (at temperatures approaching 100° and in absence of catalyst), the same relationship is preserved also in oxidation by hydrogen peroxide [3].
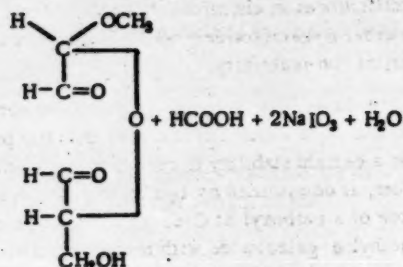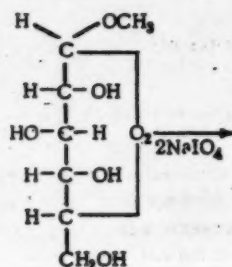
For the characterization of the reactivities of the hexosides toward acid solutions of sodium metaperiodate we used both methods. When using polarimetry, we determined the relative changes in the specific rotation of 2.5% aqueous solutions of the hexosides at 20° and 25°.

The results obtained at 25° are presented in Fig. 1 in the form of curves for the dependen of $[a_D^{20}]_{rel}$ on time.

These results show that, in the initial period of oxidation, methyl a-galactoside is more reactive than methyl a-glucoside. Methyl a-galactosiduronic acid occupies an intermediate position. The results were confirmed and extended by the further results obtained by the determination of formic acid, in which the reactivity of the hexoside at a given moment was characterized by the number of moles of formic acid yielded by one mole of the hexoside from the beginning of the reaction up to that moment.

The reactivities of hexosides toward sodium metaperiodate were determined both in acid (pH 4.2) and in alkaline (pH 11-12) media at 20°. In the determination of the reactivities of methyl a-glucoside and methyl a-galactoside in acid medium at various concentrations of oxidant (2 and 4 moles per mole of hexoside) and of substance undergoing oxidation, appreciable differences between the reactivities of the hexosides were always found during the whole of the time (60 minutes) for which reaction was allowed to continue (Figures 2, 3, and 4). It was found also that the reactivities of the hexosides increase with increase in concentration of oxidant and with diminution in the concentration of the substance undergoing oxidation.

993

By the use of the same method we compared the reactivities of methyl a-glucoside and methyl a-galactoside with that of methyl a-galactosiduronic acid in an alkaline medium. It was found that, in the initial period of oxidation, methyl a-galactosiduronic acid is more prone to oxidation than methyl a-glucoside, but less prone that methyl a-galactoside (Fig. 5).

The comparative study of the reactivities of methyl a-glucoside, methyl a-galactoside, and methyl a-galactosiduronic acid toward hydrogen peroxide was carried out only in an alkaline medium (pH 11-12) at 95°. In this case the reactivities were characterized only by formic acid determinations, the polarimetry method being inapplicable owing to the possibility of the formation of a complex mixture of products, including some having a rotatory power of opposite sign.

The hexoside-oxidation reaction was carried out at different relative concentrations of oxidant (2 and 4 moles of hydrogen peroxide per mole of hexoside undergoing oxidation) and at various concentrations of the substance undergoing oxidation. The results obtained (Fig. 6) show that, although the oxidation of the hexosides by hydrogen peroxide in an alkaline medium has, kinetically (as also chemically), a different character than their oxidation by sodium metaperiodate under the same conditions, the relative reactivities of methyl a-glucoside and methyl a-galactoside remain qualitatively the same as before: methyl a-galactoside is more readily oxidized than methyl a-glucoside.

When the reactivities of methyl a-glucoside and methyl a-galactoside are compared with that of methyl a-galactosiduronic acid, it will be seen that, in the initial period of oxidation (10-15 minutes), methyl a-galactosiduronic acid occupies an intermediate position. As oxidation proceeds further, methyl a-galactosiduronic acid becomes less reactive than methyl a-glucoside (Fig. 7). This fact was confirmed several times in comparative oxidations of methyl a-glucoside and methyl a-galactosiduronic acid at three different hexoside concentrations (0.25%, 0.125% and 0.0625%).

Hence, as a result of this comparative investigation of the reactivities of methyl a-glucoside, methyl a-galactoside, and methyl a-galactosiduronic acid in oxidation reactions with sodium metaperiodate and hydrogen peroxide, we reach the conclusion that these hexosides have different reactivities as a result of their differences in chemical structure. When, in fact, we compare the reactivities of methyl a-glucoside and methyl a-galactoside — which differ only in the configuration at C-4 — we see the effect of diastereoisomerism on reactivity.

It follows from a comparison of the reactivities of methyl a-galactoside and methyl a-galactosiduronic acid in the same oxidation reactions that the presence in the molecule of the electronegative carboxyl group confers a certain stability to oxidation on the molecule. The reactivity of methyl a-galactosiduronic acid, therefore, is determined by two factors that act in opposite directions — the spatial configuration at C-4 and the presence of a carboxyl at C-6. In this lies the cause of its intermediate position between methyl a-glucoside and methyl a-galactoside with respect to ease of oxidation. An exception occurs in the case of hydrogen peroxide oxidation, in which the difference in reactivity between methyl a-glucoside and methyl a-galactoside becomes negative. At present there is no explanation for this behavior, which requires further investigation.

It has been shown, therefore, that when oxidized by sodium metaperiodate, and also by hydrogen peroxide under defined conditions, methyl a-galactosiduronic acid is more reactive than methyl a-glucoside. This difference can be attributed to diastereoisomerism, and, together with the difference in physical structure between cellulose and pectic substances, it is the source of the difference in the rates of oxidation of the structural units, and therefore also the source of the difference in the rates of degradation of these polymers.

EXPERIMENTAL

1. Determination of Reactivity by the Polarimetry Method

Oxidation with Sodium Metaperiodate. A 0.25-g sample of the substance was dissolved in 5 ml of water and transferred quantitatively to a 10-ml measuring flask. The calculated amount of a saturated solution of sodium metaperiodate was added, and the mixture was made up to volume. The solution was mixed rapidly, and the micro-tube of the polarimeter was filled. The specific rotation was determined every 1-2 minutes for a period of 30 minutes from the start of the oxidation, and thereafter every 3-5 minutes (the start of the oxidation was taken to be the moment the sodium metaperiodate was added to the solution).

The specific rotation was calculated from the formula:

$$[a]_D^{20} \frac{a}{1 \cdot c} \qquad (1)$$

in which a is the angle through which the plane of polarization is turned, c is the concentration of the substance in g/cm, and l is the length of the tube (cm).

The values of $[a]_D^{20}$ for the original substances were determined in a similar way. From the values of $[a]_D^{20}$ the relative change in $[a]_D^{20}$ was calculated from the formula:

$$[a]_{D\ rel}^{20} = \frac{[a]_{D\ init} - [a]_D}{[a]_{D\ init} - [a]_{D\ fin}} \qquad (2)$$

in which $[a]_{D\ init}^{20}$ is the specific rotation of the unoxidized substance, $[a]_{D\ fin}^{20}$ is the specific rotation of the oxidized substance, and $[a]_D^{20}$ is a value of the specific rotation determined during the oxidation process.

From the values of $[a]_{D\ rel}^{20}$ so obtained, graphs showing its variation with time were pictted (Fig. 1).

2. Determination of Reactivity by the Quantitative Determination of Formic Acid

Oxidation with Sodium Metaperiodate in an Acid Medium.   An exactly weighed amount of the hexoside was dissolved in a little water (10 ml) and transferred quantitatively to a 100-ml measuring flask. The calculated amount of a saturated solution of sodium metaperiodate was added, and the mixture was shaken rapidly and placed in a thermostat at 20°. The moment at which the sodium metaperiodate was added was taken to be the time of the start of the reaction. After 3, 5, 10, 15, 20, 25, 30, 40, 50, and 60 minutes from the start of the reaction, 5 ml of the solution was transferred to a conical flask containing 10 ml of water and 0.2 ml of ethylene glycol. Addition of ethylene glycol was essential in order to destroy the excess of oxidant. The mixture was stirred for three minutes, and the formic acid present was then titrated with 0.02 N NaOH to Methyl red. At the same time, a control experiment was carried out which was identical, except that the oxidizable substance was absent; it was thus confirmed that, under the given conditions, neither ethylene glycol nor sodium metaperiodate gave an acid reaction to Methyl red.

The results of the determination were expressed as the number of moles of HCOOH yielded by one mole of the hexoside, which was calculated from the formula:

$$\frac{x \cdot a \cdot K \cdot 0.00092 \cdot M_{hex}}{(\text{weight taken}) \cdot 46} \qquad (3)$$

in which x is the number of milliliters of 0.02 N NaOH required for the titration of the formic acid in 5 ml of the reaction mixture; K is the correction factor of the 0.2 N NaOH; M_{hex} is the molecular weight of the hexoside; and a is the dilution.

Oxidation with Sodium Metaperiodate in an Alkaline Medium.   An exactly weighed amount of the hexoside was dissolved in a little water, and the solution was transferred quantitatively to a 100 ml measuring flask. To this mixture 10 ml of 0.1 N NaOH and the calculated amount of sodium metaperiodate were added. In other respects the procedure was the same as for the acid medium, but the amount of formic acid formed was determined by back-titration of the unneutralized alkali with 0.02 N HCl. A control experiment (no oxidizable substance) was carried out simultaneously. The amount of formic acid produced was determined from the difference in the volumes of 0.02 N HCl required for the titration of 5 ml in the control experiment and in the hexoside-oxidation experiment; it was calculated from the formula:

$$\frac{(y-x) \cdot a \cdot K \cdot 0.00092 \cdot M_{hex}}{(\text{weight taken}) \cdot 46} \qquad (4)$$

in which y is the number of milliliters of 0.02 N HCl required for the titration of 5 ml of reaction mixture in the control experiment, and x is the corresponding amount for the hexoside-oxidation experiment.

As the methyl ester of methyl a-galactosiduronic acid is readily oxidized in an alkaline medium, it was first hydrolyzed by the addition of the amount of alkali necessary for complete hydrolysis, followed by standing overnight. In other respects the procedure was as before.

Oxidation with Hydrogen Peroxide in an Alkaline Medium. A weighed amount of the hexoside was dissolved in 10 ml of water, the solution was transferred to a 50-ml measuring flask, 5 ml (7.5 ml in the case of methyl a-galactosiduronic acid) of 0.1 N NaOH was added, and the mixture was set aside overnight. The required amount of hydrogen peroxide was then added, the mixture was made up to the mark with distilled water and mixed carefully, and some of it was transferred to ampoules of 3-4 ml capacity. The ampoules were placed in a thermostat at 95°, and then removed, one at a time, after 3, 5, 10, 15, 20, 25, 30, 40, 50, and 60 minutes from the start of the oxidation. Each ampoule was broken into a small beaker, and 2 ml of its contents was transferred to a small conical flask, in which the excess of alkali was titrated with 0.02 N HCl to Methyl red. A control experiment (no oxidizable substance) was carried out simultaneously. From the difference in the volumes of 0.02 N HCl required for the titration of 2 ml in the control and in the hexoside-oxidation experiments, the amount of formic acid was determined (Formula 4).

SUMMARY

1. Under the conditions studied, methyl a-galactosiduronic acid was more readily oxidized than methyl a-glucoside.

2. It was shown that the difference in the reactivities of these models, and therefore of the elementary structural units of the corresponding polymers, is determined by the difference in spatial configuration at C-4 of the pyranose ring.

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POLYMERIZATION OF ISOPROPYL VINYL AND CYCLOHEXYL VINYL ETHERS
IN PRESENCE OF 2,2'-AZOBIS[2-METHYLPROPIONITRILE]

M.F. Shostakovsky, F.P. Sidelkovskaya, and E.S. Shapiro

It is known that vinyl ethers readily polymerize in presence of ionic catalysts of acidic character [1]. One of us and coworkers has recently shown that vinyl ethers are able to react also by a radical mechanism in addition and polymerization reactions. We studied the polymerization of ethyl vinyl, butyl vinyl [2], and phenyl vinyl [3] ethers in presence of 2,2'-azobis[2-methylpropionitrile]. In earlier work [4] on the addition of hydrogen sulfide to alkyl vinyl ethers it was established that ethers containing ramified and cyclic radicals show a greater tendency to react by an ionic mechanism and are more sensitive to factors that inhibit free-radical reactions.

It was considered to be of interest in this connection to investigate the polymerization of isopropyl vinyl and cyclohexyl vinyl ethers in presence of 2,2'-azobis[2-methylpropionitrile]. Initiation by the azo nitrile occurs as a result of its decomposition to form radicals [5]:

$$\underset{CN}{\overset{CH_3}{\underset{CH_3}{C}}} - N = N - \underset{CN}{\overset{CH_2}{\underset{CH_3}{C}}} \xrightarrow{t^\circ} 2 \underset{(I)\ CN}{\overset{CH_3}{\underset{CH_3}{C}}} - {} + N_2$$
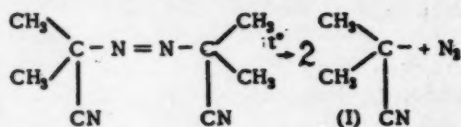
The resulting radical (I) reacts at the double bond of the vinyl ether and initiates polymerization:

$$\underset{CN}{\overset{CH_3}{\underset{CH_3}{C}}} - {} + nCH_2 = CHOR \rightarrow \underset{CN}{\overset{CH_3}{\underset{CH_3}{C}}} - [CH_2 - \underset{OR}{CH}]_{n-1} - CH_2 - \underset{OR}{CH} -$$
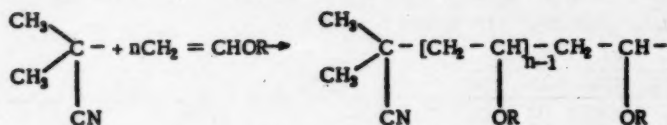
The termination of the growing chain comes about as a result of either the elimination of a hydrogen atom or acetal formation.

The polymerization of cyclohexyl vinyl and isopropyl vinyl ethers was carried out in sealed tubes in presence of 0.1-5% of initiator at 40°, 60°, and 80°. The principal results obtained are shown in Table 1.

With the object of purifying the polymers, attempts were made to reprecipitate them from solution. Experiments were carried out on poly[isopropyl vinyl ether], but we were unable to bring about reprecipitation since the material is readily soluble in almost all organic solvents (Table 2). Water is a precipitant, but it precipitates the initiator at the same time.

The polymers of isopropyl vinyl ether, which were sticky viscous liquids, were therefore not purified and were not characterized further. Poly[cyclohexyl vinyl ether], like most alkyl vinyl ether polymers, is soluble in benzene and ether, but insoluble in the lower alcohols. It was therefore purified by reprecipitation with alcohol from its solution in ether. This process yielded slightly colored transparent solid polymers, which were readily ground into fine powders. In spite of the fact that the cyclohexyl vinyl ether polymers obtained were solids, their molecular weights were relatively low. However, they melted at only 47-50°.

An examination of Table 1 indicates that, under like conditions, cyclohexyl vinyl ether polymerizes much more readily than isopropyl vinyl ether. Also, the effect of temperature is more marked in the polymerization of the cyclohexyl ether: both polymers are formed in low yield at 40°, and with rise in temperature the yield of poly[cyclohexyl vinyl ether] increases appreciably, whereas that of poly[isopropyl vinyl ether] remains substantially unchanged. For both ethers there is an increase in the yield of polymer as the concentration of initiator increases.

It is very interesting to compare the reactivities of cyclohexyl vinyl and phenyl vinyl ethers (see Tables 1 and 3).

TABLE 1

Polymerization of Isopropyl Vinyl and Cyclohexyl Vinyl Ethers in presence of 2,2'-Azobis[2-methylpropionitrile] (130 hours)

Expt. No.	Ether	Amount of azo nitrile (%)	Temperature (°C)	Yield of polymer (%)		Characteristics of reprecipitated polymer		
				not reprecipitated	reprecipitated	Molecular weight	N content (%)	M. p. (°C)
1	C₆H₁₁	0	60	0.1	—	—	—	—
2	Ditto	0.1	60	13.9	10.1	1374 1440	Traces	47-48
3	"	1	60	29.4	22.0	1299 1289	Traces	47-48
4	"	1	40	12.6	—	—	—	—
5	"	1	80	25.5	—	—	—	—
6	"	3	60	49.0	40.0	1163	0.675 0.635	47-49
7	"	5	60	52.3	44.0	1124 1072	0.957 0.956	47-48
8	i-C₃H₇	0.1	60	4	—	Attempts to reprecipitate were not successful		
9	Ditto	1	60	11.4	—			
10	"	1	40	12.6	—			
11	"	1	80	9.2	—			

TABLE 2

Solubility of Polymers Obtained

Polymer	Solvent								
	Water	Methanol	Ethanol	Butyl alcohol	Methylene chloride	Carbon tetra-chloride	Benzene	Ether	Petroleum ether
Poly[isopropyl vinyl ether]	—	+	+	+	+	+	+	+	+
Poly[cyclohexyl vinyl ether]	—	—	—	+	+	+	+	+	+

TABLE 3

Polymerization of Phenyl Vinyl Ether in presence of 2,2'-Azobis[2-methylpropionitrile] *

Expt. No.	Amount of initiator (%)	Temperature (°C)	Time (hours)	Yield of polymer (%)	Molecular weight	N content (%)	Formula of polymer
1	1	50	280	7.2	787	2.5	$(C_8H_8O)_5C_8H_{12}N_2$
2	4	60	100	14.0	805	1.8	$(C_8H_8O)_6C_8H_{12}N_2$

* Results of M.F. Shostakovsky and A.V. Bogdanova [3].

These results show that, in presence of 2,2'-azobis[2-methylpropionitrile], cyclohexyl vinyl ether polymerizes more readily than phenyl vinyl ether. In the latter case the authors concluded [3] that the azo nitrile not only activates the polymerization of the ether, but also terminates it, so that the polymer is built up from 5-6 molecules of phenyl vinyl ether and two residues of the azo nitrile [the radical (I)]:

$(\underline{n} = 5 \text{ or } 6)$.

This phenomenon was not observed in the polymerization of cyclohexyl vinyl ether. The nitrogen content of the polymer is very low (Table 1), and, although the nitrogen content increases somewhat with increase in the concentration of initiator, it remains too low to provide a basis for any definite conclusions (in view of the accuracy with which the analysis can be made). Hence, the character of the polymerization and chain-termination processes is somewhat different for cyclohexyl vinyl ether than for phenyl vinyl ether— a fact that is to be explained mainly by the absence of double bonds in the ring.

In a comparison of free-radical polymerization (in presence of the azo nitrile) and ionic polymerization (in presence of $FeCl_3 \cdot 6H_2O$), as observed in isopropyl vinyl and cyclohexyl vinyl ethers, it should be noted that in free-radical polymerization the yields and molecular weights of the polymers are lower than in ionic polymerization. In the latter case the yield of poly[isopropyl vinyl ether] is about 60% and its molecular weight is 4500 and the yield of cyclohexyl vinyl ether is about 95% and its molecular weight is 1500 [6]; also both polymers are viscous liquids. On the other hand, as already pointed out, in the polymerization of cyclohexyl vinyl ether in presence of the azo nitrile, brittle solid polymers are obtained, in spite of the fact that their molecular weights do not exceed 1300. This peculiar behavior is evidently associated, on the one hand, with the nature of the original monomer and, on the other, with the character of the initiation of the polymerization process. It follows from the above that vinyl ethers, when polymerized by the free-radical mechanism in presence of 2,2'-azobis[2-methylpropionitrile], give polymers of comparatively low molecular weight, the yields and properties of these polymers being dependent on the structure of the vinyl ether used.

EXPERIMENTAL

The starting materials were 1) isopropyl vinyl ether, a commercial product purified by the standard procedure of the Vinyl Compounds Laboratory, b.p. 55-56°, n_D^{20} 1.3860; 2) cyclohexyl vinyl ether, prepared by the vinylation of cyclohexanol in an autoclave by Favorsky and Shostakovsky's method, b.p. 42° (11 mm), n_D^{20} 1.5180 [7]; and 3) 2,2'-azobis[2-methylpropionitrile], which was purified by recrystallization from methanol.

Weighed amounts of catalyst and vinyl ether (20-30 g) were placed in a tube, which was sealed and heated in a thermostat for the required period of time. The tubes were then cooled and opened, and their contents were vacuum-distilled in order to remove monomer. For cyclohexyl vinyl ether, the evacuation was carried out at a residual pressure of 5-6 mm until the residual polymer attained constant weight (the bath temperature was not allowed to exceed that used in the polymerization experiment). The reaction product obtained from isopropyl vinyl ether was first evacuated to 30-40 mm in order to remove most of the monomer, and the residual polymer was dried to constant weight at 5-6 mm. The principal results obtained are given in Table 1. Polymers No. 2,3,6, and 7 were reprecipitated, for which purpose they were dissolved in ether (15 g of polymer in 10 ml of ether) and precipitated with ethanol (150 ml to 10 ml of ether). The precipitated polymer was separated, washed twice with alcohol, and vacuum-dried to constant weight at 60°.

SUMMARY

1. A study was made of the free-radical polymerization of cyclohexyl vinyl and isopropyl vinyl ethers in presence of 2,2'-azobis[2-methylpropionitrile].

2. It was shown that the yields and molecular weights of the resulting polymers are dependent on the conditions of polymerization and the structure of the ether.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 83. SYNTHESIS OF POLYALKYLENECYCLOALKYLS

V.V. Korshak and G.S. Kolesnikov

No macromolecular compounds are yet known which have linear molecules consisting of alternating alkane and cycloalkane residues, i.e. of the general type $C_nH_{2n-2}C_mH_{2m}$, for example:

$$-CH \begin{array}{c} CH_2-CH_2 \\ \\ CH_2-CH_2 \end{array} CH-CH_2CH_2-$$
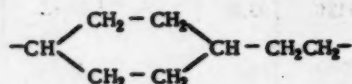
Such macromolecular carbon-chain compounds containing cyclohexane residues as have been prepared have contained these residues as side chains, not as components of the polymer chain. Such compounds include polymers of vinylcyclohexane, prepared by the hydrogenation of polystyrene [1, 2].

The preparation of macromolecular compounds having chains composed of cycloalkane and alkane residues can be effected by several methods, but all of these are very complex and consist of many stages. It is probably for this reason that no attempts have yet been made to synthesize such compounds. However, macromolecular compounds of this type can be prepared in one stage by the hydrogenation of the corresponding polyalkylenearyls. This method for the synthesis of a new class of macromolecular compounds — polyalkylenecycloalkyls — has not been suggested previously, and we therefore undertook the task of synthesizing polyalkylenecycloalkyls by this method.

In order to determine whether polyalkylenearyls can be hydrogenated like other aromatic hydrocarbons in presence of Raney nickel without being degraded, we carried out a series of experiments on the hydrogenation of various polyalkylenearyls prepared by the polycondensation of dihaloalkanes with aromatic hydrocarbons in presence of aluminum chloride and by the transarylation of diarylalkanes [3, 4].

The hydrogenation of polyalkylenearyls was carried out in cyclohexane and in mixtures of cyclohexane and benzene. It was shown also that the hydrogenation can be carried out in absence of solvent. The catalyst was prepared by the leaching of a nickel-aluminum alloy [5], and it was preserved in jars under alcohol. A definite volume of slurry, consisting of catalyst and alcohol, was taken for the hydrogenation. The following substances were hydrogenated:
poly[methylenephenyl] $(CH_2C_6H_4)n$, poly[ethylenephenyl] $(CH_2CH_2C_6H_4)n$, poly[ethylenetolyl] $(CH_2CH_2C_6H_3(CH_3))n$, poly[ethylenebiphenylyl] $(CH_2CH_2C_6H_4C_6H_4)n$, poly[ethylenenaphthyl] $(CH_2CH_2C_{10}H_6)n$, and poly[ar-ethylene-1,2,3,4-tetrahydronaphthyl] $(CH_2CH_2C_{10}H_{10})n$. The results obtained are given in Table 1.

Table 1 shows that polyalkylenearyls usually undergo hydrogenation in presence of Raney nickel, and for some of them (Experiments 2 and 3) hydrogenation is almost complete. The causes of incomplete hydrogenation may be the presence of impurities in the polyalkylenearyls and the use of hydrogenation conditions that did not correspond to the optimum conditions for the process.

The hydrogenation of poly[ethylenephenyl] can be represented by the scheme:

$$(CH_2CH_2C_6H_4)_n + 3nH_2 \xrightarrow{Ni} (CH_2CH_2C_6H_{10})_n.$$
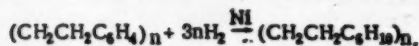
and the hydrogenation of the other polyalkylenearyls proceeds similarly.

The products formed by the hydrogenation of polyalkylenearyls are macromolecular compounds, and they preserve the original appearance, apart from color. The color of the hydrogenation products is not so deep as that of the polyalkylenearyls from which they are derived, and when hydrogenation is complete, or almost complete, the products are light yellow, or even only slightly yellowish.

TABLE 1

Hydrogenation of Polyalkylenearyls

Expt. No.	Polyalkylenearyl	Molecular weight	Hydrogenation product		Content (%)			
			Yield (%)	Molecular weight	Found		Calculated for poly[alkylene-cycloalkyl]	
					C	H	C	H
1	Poly[methylenephenyl]	1420	93.4	1620	88.27	11.27	87.43	12.57
					88.35	11.27		
2	Poly[ethylenephenyl]	2560	87.8	2890	87.19	12.82	87.19	12.81
					87.40	12.94		
3	Poly[ethylenetolyl]	3120	93.2	3300	87.45	12.32	87.02	12.98
					87.30	12.60		
4	Poly[ethylenebiphenylyl]	3540	88.1	3500	88.55	11.67	87.42	12.58
					88.42	11.50		
5	Poly[ar-ethylene-1,2,3,4-tetrahydronaphthyl]	2940	82.7	2900	88.66	11.45	87.79	12.21
					88.55	11.45		
6	Poly[ethylenenaphthyl]	2460	64.4	2540	89.77	9.88	87.79	12.21
					90.08	9.89		

It is interesting that the lightening of the color of polyalkylenearyls during hydrogenation occurs more rapidly than the growth in the extent of the hydrogenation. We attempted to estimate quantitatively the change in color occurring during the hydrogenation of polyalkylenearyls, and for this purpose we compared the colors of benzene solutions of some polyalkylenearyls with the same solutions after the hydrogenation treatment, the comparison being made with the aid of a Duboscq colorimeter.

If the change produced by hydrogenation in the intensity of the color of the polyalkylenearyl were directly proportional to the extent of hydrogenation of the aromatic cycles, then the following equation would hold:

$$c_1 \cdot h_1 = c_2 \cdot h_2 \cdot A,$$

in which c_1 is the concentration of the solution of polyalkylenearyl (basal moles per liter), h_1 is the thickness of the layer of polyalkylenearyl solution (mm), c_2 is the concentration of the solution of hydrogenated polyalkylenearyl (basal moles per liter), h_2 is the thickness of the layer of the solution of hydrogenated polyalkylenearyl, and A is a coefficient expressing the fraction of the originally aromatic cycles of the polyalkylenearyl that remain unhydrogenated. The coefficient A has the value

$$A = \frac{\Delta H_t - \Delta H}{\Delta H_t}$$

in which ΔH_t is the total change in the hydrogen content of the repeating unit of the polyalkylenearyl when it is completely hydrogenated (%), and ΔH is the observed change in the hydrogen content of the repeating unit during the hydrogenation of the polyalkylenearyl (%).

As the change in the molecular weight of the repeating unit of the polyalkylenearyl resulting from hydrogenation — particularly partial hydrogenation — is not great, c_1 and c_2 can be expressed in grams per liter for a given polyalkylenearyl. Table 2 gives values of

$$c_1 \cdot h_1; \quad c_2 \cdot h_2 \cdot A \quad \text{and} \quad \frac{c_2 \cdot h_2 \cdot A}{c_1 \cdot h_1}.$$

calculated from the results of the colorimetric measurements. It will be seen from Table 2 that in no case

is the equation $c_1 \cdot h_1 = c_2 \cdot h_2 \cdot A$ observed, which indicates the absence of direct proportionality between the intensity of the color and the extent of the hydrogenation of the aromatic cycles. We consider that the results obtained can be explained as follows. It is known that, when we pass from aromatic compounds to cycloalkanes formed from them by hydrogenation, there is a shift in the absorption spectrum toward the shorter waves. It may be expected that the conversion of phenylene groups into cyclohexylene groups will also result in a shift in the absorption spectrum toward the shorter waves.

TABLE 2

Change in Color resulting from the Hydrogenation of Polyalkylenearyls*

Polyalkylenearyl	A	$c_1 \cdot h_1$	$c_2 \cdot h_2 \cdot A$	$\dfrac{c_2 \cdot h_2 \cdot A}{c_1 \cdot h_1}$
Poly[methylenephenyl]	0.28	7.0	114.4	16.3
Poly[ethylenephenyl]	0.50	11.5	21.3	1.85
Poly[ethylenetolyl]	0.79	17.3	289.3	16.7
Poly[ethylenebiphenylyl]	0.17	4.1	87.4	21.3
Poly[ethylenenaphthyl]	0.43	1.9	283.4	149.2

* Partial-hydrogenation products of polyalkylenearyls were taken for the measurements.

Comparison of the absorption spectra of poly[ethylenephenyl] and its hydrogenation product poly-[ethylenecyclohexyl] (Figures 1 and 2) shows that hydrogenation causes the spectrum to be displaced considerably toward the ultraviolet region*. Hence, the replacement of phenylene by cyclohexylene results in a change in the absorption spectrum of the polymer. It is probable that the color of poly-[ethylenephenyl] and other polyalkylenearyls is the result of the accumulation of a large number of phenylene groups in the polymer chain. This supposition was to a certain extent confirmed by comparison of the absorption spectra of bibenzyl and diphenethylbenzene (Figures 3 and 4); these compounds were obtained by us among the products of the polycondensation of 1,2-dichloroethane with benzene in presence of aluminum chloride [3, 6]. It will be seen from Fig. 4 that replacement of a hydrogen of the phenyl radical by the phenethyl radical results in an appreciable shift of the absorption spectrum toward the nearer ultraviolet region.
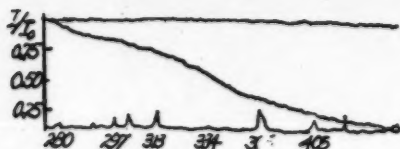

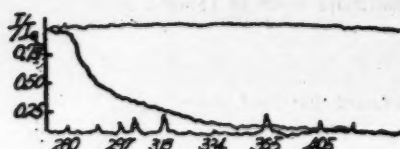Fig. 1. Absorption spectrum of poly-[ethylenephenyl]

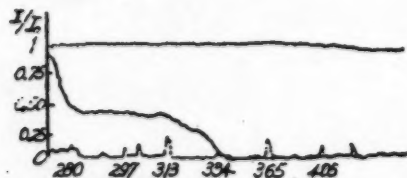Fig. 2. Absorption spectrum of poly-[ethylenecyclohexyl]
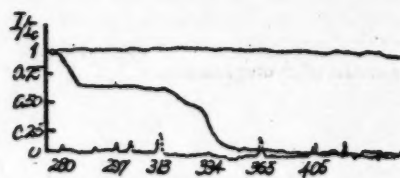

Fig. 3. Absorption spectrum of bibenzyl

Fig. 4. Absorption spectrum of diphenethylbenzene

* The absorption spectra given in this paper were determined by I.A. Palitsina, to whom we express our sincere thanks.

It is probable that the change in color associated with change in the nature of part of the polyalkylenearyl molecule (when hydrogenation is partial) may be related to the extent of hydrogenation in accordance with a law that is more complex than direct proportionality. The hydrogenation of individual phenylene groups in the polyalkylenearyl molecule may result in the partition of the polyalkylenearyl chain by cyclohexylene groups, or catenations of such groups, into short polyalkylenearyl chains. In this way the mutual effects of the phenylene groups within the chain — which are the source of the color — will be weakened, or even rendered quite ineffective.
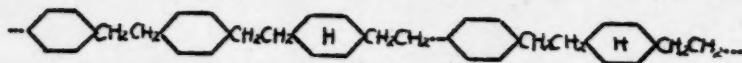
It is known that the lower members of this polymer-homologous series are not colored at all, or are very feebly colored (diphenylmethane, diphenylethane, diphenethylbenzene, and others) and the partition of the polyalkylenearyl molecule into short chains will probably result in a considerable weakening of the color, since such a molecule of irregular structure can be regarded as the sum of the individual short molecules (only from a point of view of color). Dehydrogenation of the hydrogenation product from poly[ethylenephenyl] by means of selenium gave the original poly[ethylenephenyl], which yielded terephthalic acid when oxidized. The terephthalic acid was identified as the dimethyl ester.

EXPERIMENTAL
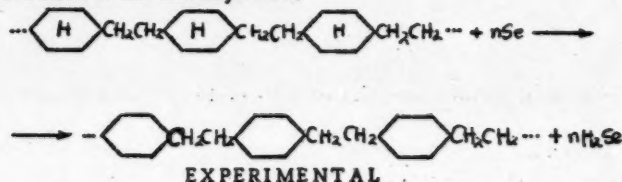
The polyalkylenearyls were hydrogenated in an electrically heated two-liter stainless-steel rotating autoclave. The polyalkylenearyl to be hydrogenated was dissolved in cyclohexane or a mixture of cyclohexane and benzene, the solution was poured into the autoclave, and Raney nickel was added in the form of a slurry with alcohol. The autoclave was closed, and hydrogen was passed in from a cylinder. Heating was at 180° for 4-5 hours. When, after the autoclave had cooled, it was found that the pressure differed greatly from its initial value, a fresh portion of hydrogen was passed in and hydrogenation was continued. When hydrogenation was complete, the autoclave was cooled, the solution of the hydrogenation product was filtered, cyclohexane was distilled from the filtrate, and the residue was heated at 300° at a residual pressure of 4-5 mm for 15-20 minutes. The molecular weights of the polyalkylenearyls and polyalkylenecycloalkys were determined viscosimetrically. The results are given in Table 1.

SUMMARY

1. It was found that the hydrogenation of polyalkylenearyls in presence of Raney nickel results in the formation of polyalkylenecycloalkyls — polymers of a new type, the chains of which contain cycloalkane and alkane residues.

2. It was shown that the hydrogenation of polyalkylenearyls is accompanied by a considerable weakening of their color.

3. Suggestions are made concerning the source of the color of polyalkylenearyls and the causes of its weakening as a result of hydrogenation.

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* Yu. I. Chizhevsky collaborated in the experimental work.

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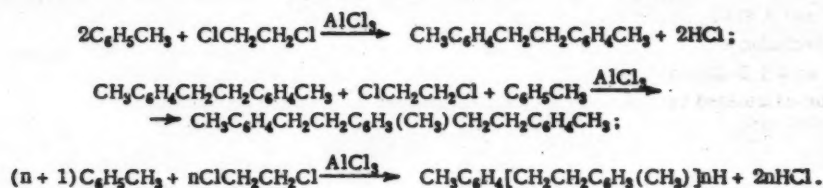
MACROMOLECULAR COMPOUNDS

COMMUNICATION 84. POLYCONDENSATION OF 1,2-DICHLOROETHANE WITH TOLUENE

G.S. Kolesnikov, V.V. Korshak, and T.A. Soboleva

Two of us with Fedorova [1] have shown that, in the condensation of chlorobenzene with 1,2-dichloro-ethane in presence of aluminum chloride, a much smaller excess of the aromatic compound is necessary for the formation of three-dimensional polymers than in the polycondensation of benzene with 1,2-dichloroethane, so that a single substituent in benzene must hinder the formation of three-dimensional polycondensational products. Continuing this investigation, we have studied the polycondensation of 1,2-dichloroethane with toluene, which, like chlorobenzene, is a monosubstituted benzene. In toluene the substituent is somewhat larger than in chlorobenzene (the radii of the substituents are 1.09 and 0.99 A, respectively) [2]. Also, in alkylations in presence of aluminum chloride, the methyl group, unlike the chlorine atom, directs a second substituent into the meta position.

In our experiments on the polycondensation of 1,2-dichloroethane with toluene in presence of aluminum chloride, the concentration of catalyst, the temperature and the duration of the reaction were kept constant. The toluene : dichloroethane ratio was varied, but the amount of toluene was kept constant. The catalyst concentration was 3 mole-% on the toluene. The experimental procedure was the same as that used for the experiments with benzene [3] and chlorobenzene [1]. When separating reaction products of low molecular weight by vacuum distillation we collected a fraction boiling up to 200° (3 mm), which consisted essentially of ar,ar'-dimethylbibenzyl, and a fraction boiling at 200-250° (3 mm), consisting mainly of bis(2-tolylethyl)-toluene. The residue of poly[ethylenetolyl] was not treated further. The formation of these products can be represented by the scheme:

$$2C_6H_5CH_3 + ClCH_2CH_2Cl \xrightarrow{AlCl_3} CH_3C_6H_4CH_2CH_2C_6H_4CH_3 + 2HCl;$$

$$CH_3C_6H_4CH_2CH_2C_6H_4CH_3 + ClCH_2CH_2Cl + C_6H_5CH_3 \xrightarrow{AlCl_3}$$
$$\rightarrow CH_3C_6H_4CH_2CH_2C_6H_3(CH_3)CH_2CH_2C_6H_4CH_3;$$

$$(n+1)C_6H_5CH_3 + nClCH_2CH_2Cl \xrightarrow{AlCl_3} CH_3C_6H_4[CH_2CH_2C_6H_3(CH_3)]nH + 2nHCl.$$

The results of the experiments on the polycondensation of 1,2-dichloroethane with toluene are shown in the table and figure.

It will be seen from the table and figure that the molecular weight of the polycondensation product increases as the excess of toluene diminishes and attains a maximum when there is a small excess of dichloro-ethane. No three-dimensional polycondensation products are formed when there is an excess of toluene and even when the reactants are taken in equimolecular proportions; a three-dimensional product is formed only when the dichloroethane is in excess. A comparison of the conditions required for the formation of three-dimensional polymer in the polycondensations of toluene and benzene [3, 4] shows that, under given conditions (catalyst concentration, duration and temperature of the reaction), the formation of such a polymer is more difficult in the case of toluene. This may be the result of steric hindrance in that the benzene nuclei in poly[ethylenetolyl] contain three substituents, whereas in poly[ethylenephenyl] they contain only two. It is interesting to note that the formation of three-dimensional polymers from toluene is even more difficult than their formation from chlorobenzene, although both compounds are monosubstituted benzenes and their potential functionalities are identical. The cause of this may lie both in the size of the substituent and in the relative positions of the three substituents in the repeating unit of the polycondensation product. It is un-likely that the sizes of the substituents can be the main cause of the less ready formation of three-dimensional

polymer by toluene, since the methyl group is only slightly larger than the chlorine atom. The main cause of this behavior must probably be sought in the structure of poly[ethylenetolyl].

In poly[chloro(ethylene)phenyl] the repeating unit has the structure:
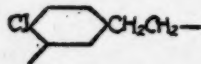
and a fourth substituent may enter the nucleus (as it must do for the formation of ramified and three-dimensional polycondensation products) in the ortho position with respect to the chlorine atom. The entry of a fourth substituent in this position is facilitated by the ortho-directing power of the chlorine atom and by the tendency of the aliphatic $-CH_2CH_2-$ bridge to direct substituents to the meta position, i.e. the ortho position with respect to the chlorine. It is probable that the structure of poly[ethylenetolyl] differs from that of poly[chloro(ethylene)phenyl].
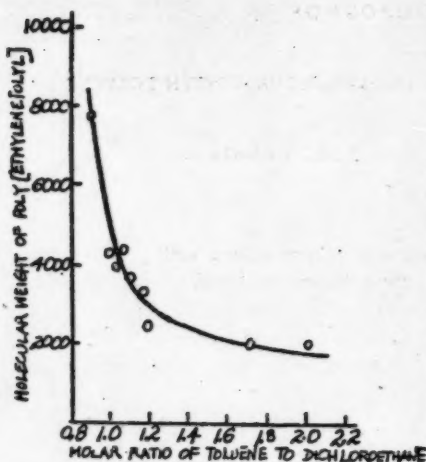
Dependence of the molecular weight of poly[ethylenetolyl] on the relative amounts of reactants.

In order to determine the structure of the polycondensation products obtained from 1,2-dichloroethane and toluene, we carried out the destructive oxidation of ar,ar'-dimethylbibenzyl, bis(2-tolylethyl)toluene, and poly[ethylenetolyl] with dilute nitric acid under pressure. Before being oxidized, dimethylbibenzyl was redistilled, and the fraction boiling at 139-140° (6 mm) was collected. The oxidation of ar,ar'-dimethylbibenzyl yielded isophthalic and terephthalic acids, identified by the melting points of their dimethyl esters, the values obtained being 64-66° for the isophthalic ester (the literature [5] gives 66-67°) and 137-139° for the terephthalic ester (the literature [6] gives 140°). Values obtained for the equivalent weight of isophthalic acid were 81.2 and 82.3 (calculated value: 83.06). The dimethyl terephthalate that we obtained showed no melting point depression in admixture with pure authentic dimethyl terephthalate. The ar,ar'-dimethylbibenzyl was therefore probably a mixture of the 3,3' and 4,4' isomers, though the possibility of the presence of 3,4'-dimethylbibenzyl in the mixture cannot be excluded — the formation of this compound was postulated by Friedel and Crafts for the reaction of toluene with 1,2-dibromoethane [7]. The analytical results for the dimethylbibenzyl were in close accord with the calculated values.

Found %: C 91.38; 91.15; H 8.69; 8.58
$C_{16}H_{18}$: Calculated %: C 91.37   H 8.63

Before being oxidized, bis(2-tolylethyl)toluene was redistilled, and the fraction boiling at 230-245° (3 mm) was collected. The analytical results for this fraction were in close accord with the calculated values.

Found %: C 91.07; 91.11; H 8.84; 8.78
$C_{25}H_{28}$. Calculated %: C 91.41;   H 8.59

The oxidization of bis(2-tolylethyl) toluene and poly[ethylenetolyl] with dilute nitric acid at 220° under pressure resulted in the isolation of a mixture of isophthalic and terephthalic acids; no benzenetricarboxylic acid could be isolated. This could be explained both by decarboxylation of any benzenetricarboxylic acid formed under the conditions of the reaction, and also by oxidation of the benzenetricarboxylic acid with rupture of the aromatic ring. When the poly[ethylenetolyl] was oxidized with dilute nitric acid (sp. gr. 1.1) at 180° under pressure, some trimesic acid was obtained, in addition to isophthalic and terephthalic acids. The trimesic acid was identified as its trimethyl ester, which melted at 141-142° (the literature [8] gives 144°). The ester obtained showed a considerable depression in melting point when

mixed with dimethyl terephthalate. The analytical results for the trimethyl trimesate were in close accord with the calculated values.

Found %: C 57.35; 57.59; H 4.68; 4.60

$C_{12}H_{12}O_6$. Calculated %: C 57.14; H 4.80

TABLE

Polycondensation of 1,2-Dichloroethane with Toluene

Molar ratio of toluene to di-chloroethane	Yield (%)			Specific viscosity of a 3% solution of poly[ethylenetolyl] in benzene	Molecular weight of poly[ethylenetolyl]
	ar,ar'-Dimethylbibenzyl	Bis(2-tolylethyl) toluene	Poly[ethylenetolyl]		
2.02	20.4	17.7	24.7	0.090	1970
1.71	14.1	11.9	55.2	0.091	1990
1.18	3.4	6.3	50.3	0.112	2440
1.16	3.1	3.7	47.6	0.152	3320
1.10	2.8	2.2	48.2	0.163	3570
1.06	3.3	3.7	45.8	0.205	4480
1.025	3.5	6.3	44.1	0.180	3940
1.00	3.8	4.6	41.1	0.196	4280
0.905	4.5*	3.9*	43.2**	0.360***	7870***

* On toluene taken.

** On toluene taken; it consists of 29.1% soluble product and 14.1% insoluble product.

*** Of soluble product.

The formation of trimesic, isophthalic, and terephthalic acids in the oxidation of poly[ethylenetolyl] indicates that this polymer contains structural units in which the aliphatic substituents are oriented meta or para to one another. Such units could be:
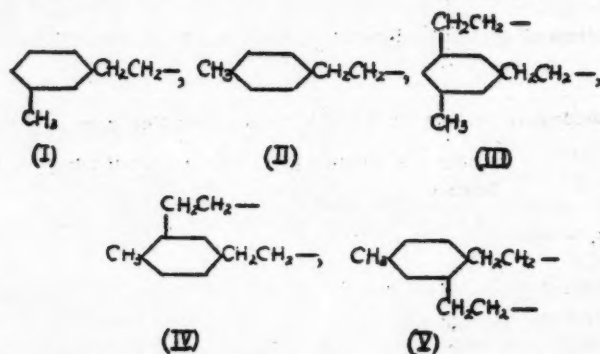
(I) and (II) can exist only as terminal groups, and their oxidation will result in the formation of isophthalic and terephthalic acids. The oxidation of (III) will give trimesic acid, but subsequent decarboxylation can then yield isophthalic acid. Oxidation of (IV) and (V) should give trimellitic acid, which however, we were unable to isolate; if it is formed at all, it is formed only in very small amount. The proportions of (IV) and (V) in the poly[ethylenetolyl] chain are probably small, but it is quite possible that they are present, since they are formed by reaction of p-ethyltoluene with 1,2-dichloroethane and toluene. It is probable that the main type of repeating unit is (III), so that poly[ethylenetolyl] differs in structure from poly[chloro(ethylene)-phenyl]. In poly[ethylenetolyl] the hydrogen atoms available for replacement under the action of dichloroethane

in presence of aluminum chloride are screened by neighboring alkyl groups; the orienting influence of the alkyl groups is also unfavorable to the further reaction of poly[ethylenetolyl] with dichloroethane, and only when there is excess of dichloroethane in the reaction mixture does the formation of ramified and three-dimensional polycondensation products become possible. Hence, the cause of the greater difficulty in the formation of a three-dimensional polymer in the polycondensation of dichloroethane with toluene in presence of aluminum chloride lies in the fact that in poly[ethylenetolyl] the substituents are predominantly arranged meta to one another, and this arrangement sterically hinders further substitution.

SUMMARY

1. A study was made of the polycondensation of 1,2-dichloroethane with toluene with formation of poly[ethylenetolyl]. The low-molecular-weight products of this reaction were ar,ar'-dimethylbibenzyl and bis(2-tolylethyl) toluene.

2. The structure of the polycondensation products formed from 1,2-dichloroethane and toluene was established.

3. It was shown that the cause of the greater difficulty with which three-dimensional polymers are formed in the polycondensation of 1,2-dichloroethane with toluene — as compared with the analogous reaction between 1,2-dichloroethane and chlorobenzene— is the steric hindrance that arises from an arrangement of substituents oriented predominantly meta to one another.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 85. POLYCONDENSATION OF 1, 2-DICHLOROETHANE WITH o-DICHLOROBENZENE

G.S. Kolesnikov and V.V. Korshak*

In studies of the polycondensation of 1, 2-dichloroethane with monosubstituted benzenes (chlorobenzene and toluene), we have already shown that the introduction of even a single substituent into the benzene nucleus greatly hinders the formation of ramified and three-dimensional polycondensation products [1, 2]. It may therefore be supposed that, with the introduction of two substituents into the benzene nucleus, the formation of ramified and three-dimensional polymers will be rendered still more difficult or may even become impossible.

We have made a study of the polycondensation of 1, 2-dichloroethane with o-dichlorobenzene in presence of aluminum chloride with the object of determining the effect of the positions of the substituents in a disubstituted benzene on the course of its polycondensation with 1, 2-dichloroethane. In order to determine the effect of the relative amounts of the reactants, we carried out a series of experiments in which the amounts of o-dichlorobenzene and aluminum chloride and the duration and temperature of the reaction were kept constant, while the amount of dichloroethane was varied over a wide range. Experiments were carried out both with an excess of dichlorobenzene and also with an excess of dichloroethane. In all experiments the catalyst concentration was 6.0 mole-% on the amount of o-dichlorobenzene. The experimental procedure was as in previous investigations [1-3]. In distilling off reaction products of low molecular weight under reduced pressure, we collected a fraction boiling up to 230° (5-6 mm), which we took to be a tetrachlorobibenzyl. The polycondensation product poly[dichloro(ethylene)phenyl] was purified by reprecipitation from a 4% benzene solution by addition of six times the volume of methanol. The molecular weight of the poly[dichloro(ethylene)phenyl] was determined viscosimetrically. The experimental results are given in the figure and in Table 1.
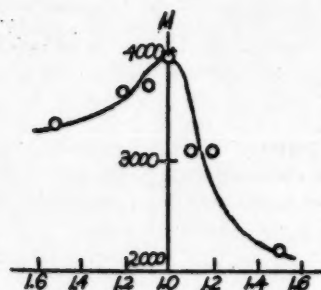
M is the molecular weight of poly[dichloro-(ethylene)phenyl], and is plotted against molar ratio of dichloroethane to dichlorobenzene (on the left) and molar ratio of dichlorobenzene to dichloroethane (on the right).

It will be seen from Table 1 and the figure that the polycondensation of 1, 2-dichloroethane with o-dichlorobenzene takes place, irrespective of which of the reactants is in excess, and no insoluble, three-dimensional polymers are formed, even when there is a considerable excess of dichloroethane. Hence, introduction of two substituents into the benzene nucleus of the aromatic reactant affects the reaction in such a way that, at low catalyst concentrations (up to 6 mole-%), of the four hydrogen of o-dichlorobenzene, only two can be replaced, the potentially quadrifunctional o-dichlorobenzene behaving, therefore, as a bifunctional compound. As the polycondensation of 1, 2-dichloroethane with o-dichlorobenzene must be regarded as a polycondensation reaction between two bifunctional compounds at this particular catalyst concentration then— in accordance with the theory of linear polycondensation [4]— the products of highest molecular weight should be obtained when equimolecular proportions of reactants are used. It will be seen from Table 1 and the figure that products of maximum molecular weight are indeed formed at a molar ratio of o-dichlorobenzene to 1, 2-dichloroethane of 1.0. The yield of macromolecular products is also a maximum at this molar ratio.

The macromolecular polycondensation products obtained from 1, 2-dichloroethane and o-dichlorobenzene

* Z. Kraineva assisted in the experimental work.

1011

are solids. Purification of poly[dichloro(ethylene)phenyl] by reprecipitation resulted only in an insignificant rise in molecular weight, which was the most pronounced in the products having the highest molecular weight. The curve given in the figure for the dependence of the molecular weight of poly[dichloro(ethylene)phenyl] on the relative amounts of reactants, unlike those found, for example, for the polycondensation of dicarboxylic acids with diamines [5] is not symmetrical. We have not found the causes of this behavior, but we can suggest the following possible explanations. We have shown that reaction of dichloroethane with poly[ethylenephenyl] in presence of aluminum chloride results in the formation of insoluble, three-dimensional products, whereas reaction of dichloroethane with poly[dichloro(ethylene)phenyl] has no effect on the molecular weight of the latter at low catalyst concentration (when the catalyst concentration is high, the formation of three-dimensional products is again found). Hence, dichloroethane is not a degrading agent for poly[dichloro(ethylene)phenyl]. On the other hand, the aromatic component of the reaction mixture will degrade the macromolecular polycondensation products.

TABLE 1.

Polycondensation of 1, 2-dichloroethane with o-dichlorobenzene

Molar ratio	Yield (%)		Molecular weight of poly[dichloro-(ethylene)phenyl]	
	sym-ar-Tetrachlorobibenzyl	Poly[dichloro-(ethylene)phenyl]	Not reprecipitated	Reprecipitated
o-Dichlorobenzene: dichloroethane				
1.50	8.6	59.0	2200	2190
1.20	4.9	66.0	3060	3100
1.10	4.0	60.1	3150	3110
1.00	3.5	68.3	3500	3920
Dichloroethane: o-dichlorobenzene				
1.11	6.0•	40.2•	3550	3720
1.22	5.3•	37.4•	3420	3640
1.52	8.7•	38.6•	3200	3340

• Yield based on o-dichlorobenzene

In the polycondensation of dicarboxylic acids with diamines or glycols, the polycondensation products undergo degradation when there is an excess of either reactant and, as a result, the curve for the dependence of the molecular weight of the polycondensation product on the relative amounts of reactants is a symmetrical one. In the polycondensation of 1, 2-dichloroethane with aromatic compounds, only the aromatic reactant can act as a degrading agent: excess of dichloroethane results not in the degradation of the macromolecular products, but in the formation of ramified and three-dimensional products— or it may have no effect at all. This may be one of the causes of the unsymmetrical form of the curve given in the figure. The lowering of the molecular weight when there is an excess of dichloroethane is probably due to the reduction in catalyst concentration brought about by the addition of a large amount of diluent (dichloroethane).

Another possible cause of the asymmetry of the curve is the occurrence of side reactions. A side reaction that may occur when there is an excess of dichloroethane is the conversion of this substance into benzene in presence of aluminum chloride and the formation of polycondensation products by reaction of the benzene with unchanged dichloroethane. Shishido and Yoshikawa [6] found that treatment of 1, 2-dichloroethane with aluminum chloride yielded benzene and m-diphenethylbenzene. We repeated Shishido and Yoshikawa's experiments and found that at 49° with a molar ratio of dichloroethane to aluminum chloride of 6.75: 1, hydrogen chloride was evolved and the reaction mixture became dark brown. The reaction mixture was treated with dilute hydrochloric acid, washed with water, and dried with calcium chloride. Unchanged dichloroethane was distilled off, and vacuum distillation then yielded a very small amount of a high-boiling substance of indefinite boiling point. The residue was a dark-colored substance, and it was found to be poly[ethylenephenyl] of

molecular weight 2510. The yield of poly[ethylenephenyl] was 19.2%, calculated on the amount of dichloro-
ethane taken, it being assumed that the reaction proceeded as follows:

$$(4n + 3)ClCH_2CH_2Cl \xrightarrow{AlCl_3} H(C_6H_4CH_2CH_2)_nC_6H_5 + (8n + 6)HCl.$$
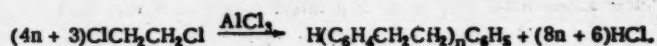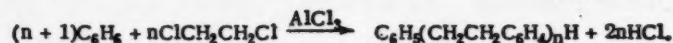
For convenience of calculation we assume that four molecules of dichloroethane give one repeating unit
of poly[ethylenephenyl]. The poly[ethylenephenyl] was identified by oxidation at the boil with chromic acid
mixture to yield terephthalic acid, identified as its methyl ester, m.p. 139-140°, undepressed by admixture
with pure authentic dimethyl terephthalate.

The first stage of the reaction is probably the formation of benzene:

$$3ClCH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_6 + 6HCl.$$
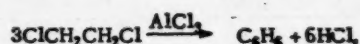
which then reacts with dichloroethane with formation of poly[ethylenephenyl]:

$$(n + 1)C_6H_6 + nClCH_2CH_2Cl \xrightarrow{AlCl_3} C_6H_5(CH_2CH_2C_6H_4)_nH + 2nHCl.$$

Thus, when the dichloroethane is in excess, not only the main polycondensation reaction will occur
with formation of poly[dichloro(ethylene)phenyl], but also, possibly, a reaction leading to the formation of
poly[ethylenephenyl]. This side reaction can also distort the course of the curve shown in the figure.
Naturally, when the aromatic reactant is in excess, this reaction does not occur, or occurs only to a very slight
extent.

When the catalyst concentration is increased to 12.0 mole-% (on the amount of o-dichlorobenzene), the
character of the dependence of the molecular weight of poly[dichloro(ethylene)phenyl] on the relative amounts
of the reactants is unaffected, and the molecular weight rises as the proportions approach equimolecular values.
The results for the polycondensation of dichloroethane with o-dichlorobenzene in presence of 12.0 mole-% of
aluminum chloride are given in Table 2.

TABLE 2

Polycondensation of 1, 2-Dichloroethane with o-Dichlorobenzene

Molar ratio of o-dichlorobenzene to dichloroethane	Yield (%)		Molecular weight of poly[dichloro-(ethylene)phenyl]	
	sym-ar-Tet-rachlorobi-benzyl	Poly[dichloro-(ethylene)phenyl]	Not reprecipi-tated	Reprecipitated
1.20	5.2	71.3	2690	3360
1.10	3.6	68.0	3510	4070
1.00	1.9	66.3	3510	5590

In order to determine the effect of catalyst concentration on the course of the polycondensation of di-
chloroethane with o-dichlorobenzene, two series of experiments were carried out. In each series all of the
experimental conditions were constant with the exception of the catalyst concentration, which was varied.
One series was carried out with an excess of o-dichlorobenzene, and the other with an excess of dichloroethane.
The results are given in Tables 3 and 4.

Table 3 shows that, when o-dichlorobenzene is in excess and the catalyst concentration is low, the
polycondensation reaction does not occur. When the catalyst concentration is increased, polycondensation
occurs with formation of poly[dichloro(ethylene)phenyl], the molecular weight of which rises with increase in
catalyst concentration.

The effect of catalyst concentration is somewhat different when the 1, 2-dichloroethane is in excess, as
can be seen from Table 4. At low catalyst concentration polycondensation does not go readily and the yield of

poly[dichloro(ethylene)phenyl] is low. Increase in catalyst concentration results in increase in the yield of poly[dichloro(ethylene)phenyl] and an increase also in its molecular weight. When a certain concentration of catalyst is attained the formation of soluble polycondensation products is accompanied by the formation of an appreciable amount of infusible, insoluble, three-dimensional polymers. It is interesting to note that the formation of insoluble three-dimensional polymers is accompanied by a fall in the molecular weight of the soluble polymeric product. The explanation of this may be that the cross-linking reaction occurs in the first place at the expense of the longer molecules, as shown previously by the present authors in collaboration with Soboleva [7]. The formation of three-dimensional polymers is accompanied also by a reduction in the yield of sym-ar-tetrachlorobibenzyl.

TABLE 3

Polycondensation of 1,2-Dichloroethane with o-Dichlorobenzene

Catalyst concentration in mole-%			Yield (%)		Molecular weight of poly[dichloro-(ethylene)phenyl]	
on dichlorobenzene	on dichloroethane	on dichloroethane + dichlorobenzene	sym-ar-Tetrachlorobibenzyl	Poly[dichloro-(ethylene)phenyl]	Not reprecipitated	Reprecipitated
1.50	1.80	0.82	2.2	–	–	–
3.00	3.60	1.63	2.9	32.8	2690	2740
6.00	7.20	3.27	4.9	66.0	3060	3100
12.00	14.40	6.55	5.2	71.3	2690	3360

TABLE 4

Polycondensation of 1,2-Dichloroethane with o-Dichlorobenzene (molar ratio of dichloroethane to dichlorobenzene = 1.52)

Catalyst concentration in mole-%			Yield (%)*		Molecular weight of poly[dichloro-(ethylene)phenyl]	
on dichlorobenzene	on dichloroethane	on dichloroethane + dichlorobenzene	sym-ar-Tetrachlorobibenzyl	Poly[dichloro-(ethylene)phenyl]	Not reprecipitated	Reprecipitated
3.00	1.97	1.19	3.7	11.7	3010	3150
6.00	3.94	2.38	8.7	38.6	3200	3340
7.50	4.93	2.97	7.2	49.4	4250	4830
12.00	7.89	4.76	4.5	92.7**	2930***	3370***

* Yields calculated on amount of o-dichlorobenzene taken.

** Including 74.1% of three-dimensional polymer and 16.6% of soluble polymer

*** Of the soluble product

The polycondensation of 1,2-dichloroethane with o-dichlorobenzene in presence of aluminum chloride can be represented as follows:

$$(n + 1)C_6H_4Cl_2 + nClCH_2CH_2Cl \xrightarrow{AlCl_3}$$

$$\longrightarrow H(Cl_2C_6H_2CH_2CH_2)_nC_6H_3Cl_2 + 2nHCl.$$
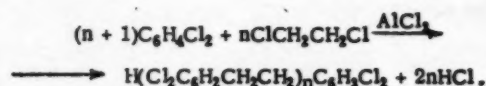
The repeating unit of the polycondensation product should have the composition $C_6H_2Cl_2CH_2CH_2$, corresponding to a chlorine content of 40.98%. Chlorine determinations on the macromolecular polycondensation product obtained gave values of 36.25% and 37.08% (average values). The difference between the experimentally found and calculated chlorine contents is outside the limits of experimental error. The low chlorine content was associated with high carbon and hydrogen contents, the experimentally determined values being 59.52, 58.59% and 4.36, 4.89%, respectively, and the corresponding calculated values 55.52% and 3.50%.

We consider that the observed departure of the composition of the polycondensation products from the calculated value may be explained by the transfer of chlorine atoms from one aromatic compound or polycondensation product to another in presence of aluminum chloride. Halogen-transfer reactions of this sort have been described in the literature. Thus, Dumreicher [8] observed the formation of dibromobenzene and benzene when bromobenzene was heated with aluminum chloride. Friedel and Crafts [9] observed chlorine transfer in the methylation of o-dichlorobenzene in presence of aluminum chloride: the main reaction products were hexamethylbenzene and trichloromesitylene. Treatment of p-dibromobenzene with aluminum chloride gave a mixture of bromobenzene, m- and p-dibromobenzenes, and two tribromobenzene isomers [10]. Roux [11] observed the formation of naphthalene, 2-bromonaphthalene, and dibromnaphthalenes when 1-bromonaphthalene was heated with aluminum chloride. Halogen transfer in presence of aluminum chloride has been observed in many other substances [12-14].

It is therefore quite probable that the polycondensation process may be accompanied by halogen redistribution with the result that the chlorine content of the polycondensation product formed from 1,2-dichloroethane and o-dichlorobenzene will be reduced. The resulting polychlorobenzene is apparently distilled off with the ar-tetrachlorobibenzyl during the vacuum distillation.

With the object of determining the structure of the polycondensation product formed from 1,2-dichloroethane and o-dichlorobenzene, we carried out its destructive oxidation. Attempts to oxidize it with boiling chromic acid mixture and with boiling dilute nitric acid at atmospheric pressure were unsuccessful. We succeeded in oxidizing it with dilute nitric acid (sp.gr. 1.1) at 220-250° and at 65-80 atm pressure. As a result of the oxidation an acid melting at 196-198° was obtained. Its equivalent weight was determined (duplicate results: 116.5 and 119.0), and the values obtained indicated that it was one of the dichlorobenzenedicarboxylic acids (calculated equivalent weight: 117.5). Values of 30.34 and 30.48% were found for the chlorine content, which are in close accord with the value calculated for a dichlorobenzenedicarboxylic acid (30.18%). The melting point of the acid corresponds to that of 4,5-dichlorophthalic acid, which melts at about 200° [15].

On the basis of the structure of the oxidation product, it may be deduced that the polycondensation product formed from 1,2-dichloroethane and o-dichlorobenzene consists mainly of repeating units of the following structure:
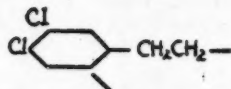
and it may be called poly[4,5-dichloro-2-ethylenephenyl]. Such a structure is in accord with the orienting effects of the substituents: each aliphatic residue is in the para position to a chlorine atom.

From the distillate obtained in the vacuum distillation — which we had assumed to be a symmetrical ar-tetrachlorobibenzyl — we isolated a substance which, after recrystallization from methanol, melted at 97-98°. Values found for its chlorine content were 44.81 and 44.93%, and the chlorine content calculated for $C_{14}H_{10}Cl_4$ is 44.32%. No symmetrical ar-tetrachlorobibenzyls have been described in the literature, but our product appeared to be 3,4,3',4'-tetrachlorobibenzyl, for only this isomer, reacting with dichloroethane and o-dichlorobenzene, could give a polymer having the repeating unit
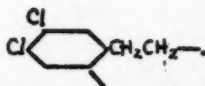
The assumed structure of the tetrachlorobibenzyl was confirmed by the results of the oxidation of the compound. The product obtained by oxidizing it with chromic anhydride in glacial acetic acid contained chlorine, was soluble in alkali, and melted at 195-196°. The literature gives a melting point of 203° for 3,4-dichlorobenzoic acid [16] and 166° for 2,3-dichlorobenzoic acid [17]. Values obtained for the chlorine content were 36.31 and 36.44%, and the calculated value for $C_7H_4O_2Cl_2$ is 37.13%.

SUMMARY

1. A study was made of the polycondensation of 1, 2-dichloroethane with o-dichlorobenzene, and the principal laws governing the process were established.

2. It was found that, when the catalyst concentration is low, o-dichlorobenzene behaves as a bifunctional compound, in spite of the fact that its potential functionality is four.

3. The structure of the polycondensation products formed from 1, 2-dichloroethane and o-dichlorobenzene was determined.

4. It was found that treatment of 1, 2-dichloroethane with aluminum chloride resulted in the formation of poly[ethylenephenyl].

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 86. DETERMINATION OF THE MOLECULAR WEIGHTS OF POLYAMIDES FROM THE VISCOSITIES OF THEIR SOLUTIONS IN CRESOL AND IN METHANOL

V.V. Korshak and S.A. Pavlova

The molecular weights of polymers can be determined rapidly and accurately by the viscosity method so long as the method has been satisfactorily calibrated against some other method of determining molecular weights. There is no theory in existence that would directly relate the results of viscosity measurements on polymers with the molecular weights of the polymers. Staudinger's formula $[\eta] = kM$ [1], as later experimental investigations have shown, is not always valid, being only a special case of some more general law. It is therefore necessary to turn to absolute methods of measurement, such as osmometry, cryoscopy, sedimentation in the ultracentrifuge, light scattering, etc.

We were faced with the problem of determining the empirical relationship between the molecular weights of polyamides and the viscosities of their dilute solutions. The available data on this matter derive from the investigations of Staudinger [2], who studied this relationship for solutions of a polyamide in cresol. The molecular weight of the original polyamide was determined by the osmotic pressure method. On the basis of his results, Staudinger proposed the formula $Z_\eta = 1.2 \cdot 10^{-4} n$. relating the viscosity number Z_n with the number $\underline{n}$ of repeating units in the polymer chain. All measurements were done at finite concentrations without extrapolation to infinite dilution. The molecular weights of the polymers studied by Staudinger were in the range 6600-8600. This formula is widely used, even at the present time. Its defects include, first, the derivation of the formula for molecular weights which are in the low region and cover too short a range and second, its derivation on the basis of data obtained at a finite concentration. Since these investigations of Staudinger were published, many further studies have been made of the viscosities of dilute solutions of polymers and their dependence on the molecular weights of the polymers [3-7].

It was found that this relationship cannot be expressed by the simple Staudinger formula for a wide range of molecular weights and is expressed more satisfactorily by $[\eta] = KM^a$ K and $\underline{a}$ being empirical constants [8]. Experiment showed that $\underline{a}$ varies among various polymer-solvent systems from 0.5 to 1.5. Many attempts have been made to elucidate the physical significance of this formula. These theoretical investigations amount to the use of various model concepts to establish the relationship between the volume occupied by the macromolecule and its hydrodynamic interaction with a stream of solvent, as affected by the degree of convolution of the macromolecule [6,7]. It was found that, for a highly convoluted polymeric chain, such that the stream of solvent cannot penetrate it but can only flow around its surface, $\underline{a}$ will be 0.5 (i.e. the viscosity of the solution will be proportional to the square root of the molecular weight of the dissolved polymer). As the structure of the convoluted ball formed by the macromolecule becomes more open and becomes more penetrable by solvent, $\underline{a}$ increases, attaining the value of unity when the macromolecule is fully accessible, so that the formula $[\eta] = KM^a$ is transformed into Staudinger's formula. The fact that values of $\underline{a}$ greater than unity are found experimentally has not yet been explained. The study of viscosity can, to a certain extent, give an idea of the form of the macromolecule in the solution and its size.

Staudinger, and also other authors, proposed another formula, which was found to be valid over a wider range of molecular weights. The physical significance of this formula $[\eta] = KM + J$ has not been elucidated. This formula has two empirical constants, K and J [9].

Our object in this investigation was to determine the relationship of viscosities of solutions of a polymer in cresol and in methanol to the molecular weight of the polymer. We considered that it was essential to extend the range of molecular weights for which the empirically determined relationship would be valid. As indicated above, Staudinger's formula was derived for polymers having molecular weights of not above 8600, whereas the polyamides that have attracted the greatest practical interest and have been

most extensively used have higher molecular weights in the range 15,000-25,000. It was of interest also to compare the two formulas cited above in order to determine which of them gives the better representation of the relationship found.

<div align="center">

EXPERIMENTAL
</div>

The polymers taken for investigation were fractions derived from some samples of mixed polyamide, the preparation and fractionation of which have been described previously [10]. The molecular weights of these fractions were determined by a method based on measurements of sedimentation in the ultracentrifuge and of diffusion, which has also been described in previous papers [10].

Viscosity Measurements

The viscosities of solutions of the polyamide were determined in cresol and in methanol at various concentrations. The measurements were made in an Ostwald viscometer at $20 \pm 0.005°$. The solvents cresol and methanol — were not subjected to any special purification process. Tables 1 and 2 give the results of the measurements and give also reduced viscosities (η/c) extrapolated to infinite dilution by the method of least squares. Table 3 gives the results of viscosity measurements in methanol at a concentration of 5 g/liter.

TABLE 1

Viscosities of Polyamide Fractions in Cresol

M 46,600		M 21,700		M 17,600		M 27,500		M 58,500	
c g/liter	η/c	c g/liter	η/c	c g/liter	η/c	c g/liter	η/c	c g/liter	η/c
2.28	0.385	5	0.160	5	0.100	5	0.235	5	0.540
1.82	0.378	5	0.163	5	0.100	5	0.241	5	0.510
1.36	0.385	4	0.169	4	0.097	4	0.230	4	0.485
0.91	0.378	4	0.158	4	0.099	4	0.231	4	0.485
0.46	0.351	3	0.157	3	0.095	3	0.216	3	0.460
		3	0.150	3	0.096	3	0.216	3	0.462
$[\eta] = 0.375$		2	0.160	2	0.090	2	0.220	2	0.465
		2	0.144	2	0.088	2	0.205	2	0.465
		1	0.150	1	0.082	1	0.221	1	0.466
		1	0.139	1	0.080	1	0.219	1	0.451
		$[\eta] = 0.142$		$[\eta] = 0.0820$		$[\eta] = 0.179$		$[\eta] = 0.425$	

Discussion of Results

Our results show that for cresol and methanol solutions of polyamides it is not possible to find a general relationship between viscosity and concentration of the form proposed by other authors [11]:

$$\eta/c = [\eta] + k [\eta]^2 c.$$

It was, however, found to be possible to obtain an expression for the relationship between the viscosities of cresol and methanol solutions of polyamides and the molecular weights on the basis of our experimental results. The relationship that we have obtained between the intrinsic viscosity of the polyamide in cresol and its molecular weight can be expressed as follows: $[\eta] = 0.29 \cdot 10^{-6} \cdot M^{1.3}$ or $[\eta] = 8.58 \cdot 10^{-6} \cdot M - 0.0551$. For the first formula the sum of the squares of discrepancies in the experimental values is $\Sigma \Delta^2 = 0.03162$, whereas for the second it is $\Sigma \Delta^2 = 0.001848$, so that the second formula would appear to be more accurate than the first. The same is true of the results obtained at 5 g/liter.

We considered it to be desirable to find the relationship between the viscosity of the polyamide solution and the molecular weight, not only for values extrapolated to infinite dilution, but also for values obtained at a concentration of 5 g/liter. Such a relationship will make it possible to obtain the necessary data for the determination of the molecular weight from two parallel measurements without the determination of the dependence of viscosity on concentration for each sample, which is a rather arduous task:

$$(\eta/c)_{c=5} = 0.522 \cdot 10^{-6} M^{1.26} \text{ or } (\eta/c)_{c=5} = 9.5 \cdot 10^{-6} M - 0.0468; \ \Sigma\Delta^2 = 0.001976; \ \Sigma\Delta^2 = 0.00099.$$

However, plotting of Staudinger's results for the viscosity of a polyamide in cresol in Figures 1 and 2 showed that for the first variant these points lie very satisfactorily between the curves calculated for the $c =$ and $c = 5$ g/liter formulas; for the second variant the discrepancy is too great.
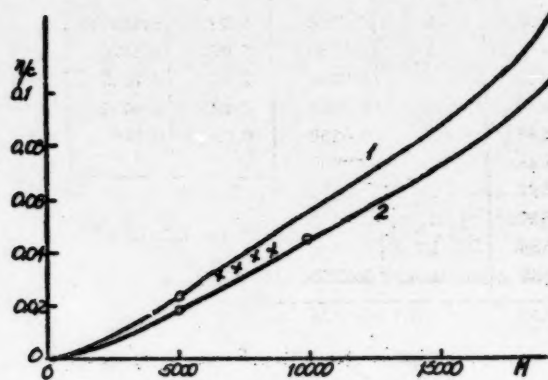

Fig. 1. 1 - curve calculated from the formula $(\eta/c)_{c=5} = 0.25 \cdot 10^{-6} M^{1.26}$; 2 - curve calculated from the formula $[\eta] = 0.29 \cdot 10^{-6} M^{1.30}$; x − Staudinger's results
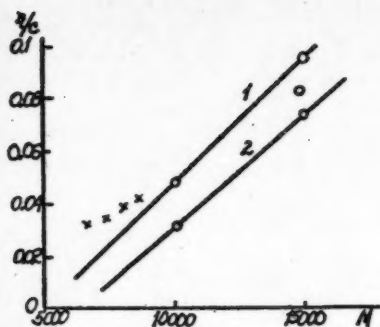

Fig. 2. 1 - curve calculated from the formula $(\eta/c)_{c=5} = 9.5 \cdot 10^{-6} M - 0.0468$; 2 - curve calculated from the formula $[\eta] = 8.6 \cdot 10^{-6} M - 0.055$; x − Staudinger's results

We can consider it to be established, therefore, that for the wide range of molecular weights investigated (6600-58500), the formula in which M is raised to a power is the best expression of the relationship sought.

For methanol solutions, the relationship between viscosity and molecular weight can be expressed by the formulas:

$$[\eta] = 5.2 \cdot 10^{-6} M^{0.9} \text{ and } [\eta] = 1.55 \cdot 10^{-6} M + 0.0084$$

$$(\eta/c)_{c=5} = 3.9 \cdot 10^{-6} M^{0.96} \text{ and } (\eta/c)_{c=5} = 2.10 \cdot 10^{-6} M + 0.011.$$

In this case the two variants are found to be equally accurate, so that either may be used with success over the range of molecular weights studied.

It is interesting to consider the difference in the values of the index a in the two systems. For polyamides in methanol $a = 0.9$. The specific viscosities of solutions in methanol are very much less than those of solutions in cresol. These facts indicate that, in methanol, the polyamide macromolecule has the form of a rather compactly coiled ball, in agreement with our earlier results in an investigation of sedimentation in the ultracentrifuge and diffusion. The power index for the polyamide-cresol system is $a = 1.3$, i.e. it must be supposed that, as a result of powerful solvation by cresol molecules, the macromolecule exists in a highly extended state in the solution.

TABLE 2

Viscosities of Polyamide Fractions in Methanol

M 58.500		M 27.500		M 17.600		M 75.600		M 21.700	
c (g/liter)	η/c	c (g/liter)	η/c	c (g/liter)	η/c	c (g/liter)	η/c	c (g/liter)	η/c
5	0.1291	5	0.0656	5	0.0363	5.00	0.1690	5	0.0562
5	0.1290	5	0.0646	5	0.0360	3.02	0.1526	5	0.0578
4	0.1221	4	0.0650	4	0.0345	2.18	0.1548	4	0.0548
4	0.1191	4	0.0640	4	0.0362	1.39	0.1451	4	0.0573
3	0.1172	3	0.0648	3	0.0350	0.08	0.1460	3	0.0537
3	0.1138	3	0.0648	3	0.0350			3	0.0593
2	0.1089	2	0.0597	2	0.0316			2	0.0503
		2	0.0597	2	0.0304	$[\eta] = 0.1317$		2	0.0575
1	0.1030	1	0.0586	1	0.0234			1	0.0492
1	0.1007	1	0.0585	1	0.0360			1	0.0492
$[\eta] = 0.087$		$[\eta] = 0.057$		$[\eta] = 0.028$				$[\eta] = 0.048$	

TABLE 3

Viscosities of Polyamide Fractions in Methanol at a Concentration of 5 g/liter

Molecular weight	$(\eta/c)_{c=5}$*	Molecular weight	$(\eta/c)_{c=5}$*
75,500	0.173	22,800	0.048
58,500	0.128	22,430	0.061
42,160	0.125	21,960	0.056
40,060	0.116	21,700	0.058
29,200	0.064	17,600	0.036
28,450	0.070	16,330	0.054
27,500	0.066	8,550	0.015
26,440	0.070	3,110	0.016
23,200	0.056		

TABLE 4

Viscosities of Polyamides in Cresol from Staudinger's Paper [2]

c (g/liter)	Z_η	Molecular weight
4.07	0.0322	6600
3.97	0.0345	7300
3.14	0.0388	8000
2.45	0.0404	8600

* $(\eta/c)_{c=5}$ is the reduced viscosity at a concentration of 5 g/liter.

SUMMARY

1. A study was made of the relationship between the viscosities of dilute solutions of polyamides in cresol and the molecular weights of the polyamides. The relationship found can be expressed by the formulas: $[\eta] = 0.29 \cdot 10^{-6} M^{1.3}$ or $[\eta] = 8.58 \cdot 10^{-6} M - 0.055$.

2. A study was made of the relationship between the viscosities of dilute solutions of polyamides in methanol and the molecular weights of the polyamides. The relationship found can be expressed by the formulas: $[\eta] = 5.2 \cdot 10^{-6} M^{0.9}$ or $[\eta] = 1.55 \cdot 10^{-6} M + 0.0084$.

3. It was found that the formula in which M is raised to a power expresses the relationship between the viscosity of a polymer solution and the molecular weight of the polymer better than the Staudinger formula with a constant term.

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POLYCONDENSATION OF GLYCINE ETHYL ESTER

V.V. Korshak, K.T. Poroshin, and T.D. Kozarenko

In a previous paper [1] we have shown that the presence of various acidic substances (organic and inorganic) can greatly affect the polycondensation reactions of esters of DL-alanine. At the same time it was pointed out that the regularities observed in this reaction can be extended also to the esters of other α-amino acids. In this connection, it was of interest to study this process in greater detail for glycine esters, for it is known that in the polycondensation reaction they give products consisting mainly of esters of polypeptides [2], cyclic dimers (piperazinediones) being present only in very small amount. It was natural, therefore, to pay attention not only to the kinetics of the polycondensation of the glycine esters, but also to the properties of the resulting mixture of polyglycine and piperazinedione Particular attention was directed to the question of the effect of various factors on the amount of piperazinediones formed. Although there is a considerable literature on this matter [3], there is as yet no clear information on the relative amounts of piperazinediones and polymers in the polycondensation products obtained from esters of α-amino acids. We made use of a recently published procedure [4] for the determination of the amount of piperazinedione in the reaction mixture, and we obtained results of interest not only with respect to glycine esters, but also with respect to esters of other α-amino acids. The main subject of investigation was glycine ethyl ester. Preliminary experiments on other esters of this acid (methyl and butyl) show that the laws of the polycondensation reaction and the identity of the products are similar to those found for the ethyl ester. Only glycine methyl ester differs notably from the other esters: under given conditions its reaction rate is higher, and the amount of polycondensation products is much lower.

EXPERIMENTAL

Glycine ethyl ester was prepared by Fischer's method [5]. In order to obtain reproducible results it is very important to dry the ester thoroughly, since traces of moisture result, as we have shown, in an appreciable increase in the rate of the process studied. In order to remove moisture as completely as possible, the free glycine ester was extracted with absolute ether, and the extract was then dried for 15 days over a large amount of calcined potassium carbonate. The ether was then distilled off, and the residue was distilled under reduced pressure. A fraction of the glycine ethyl ester having a distillation range of 1-1.5° was taken for investigation.

This fraction, which was collected in a separate receiver, was poured into one-hundred times its weight of absolute ether, and was kept over a large amount of calcined potassium carbonate. It was shown that a hundredfold dilution enabled the glycine ester to be preserved almost unchanged for more than two months. Before each experiment a known weight of the ester was taken in the form of 30-40 ml of the solution, from which ether was distilled at atmospheric pressure and the monomer (the glycine ester) was distilled by the method already described [1]. Sealed tubes containing monomer and catalyst (carbon dioxide) were placed in a thermostat at the required temperature. After a period of reaction, the tubes were opened and treated as previously described [1].

The results of the experiments are given in Fig. 1. For comparison, the results for the polycondensation at 40° of glycine ethyl ester that had not been freed from moisture with calcined potassium carbonate are given (Curve I). It will be seen from Fig. 1 that the rate of the polycondensation of the dried glycine ester under the same conditions is appreciably lower (Curve III). It is noteworthy that the reaction rate at the beginning of the process (the first 2-3 hours) is much lower than in the following period (3-5 hours after the start), so that the rate curves have a pronounced inflection (at the third hour).

In order to resolve the question of whether these inflections are the result of some, at present unknown, autocatalytic process, experiments were carried out on the polycondensation of glycine ethyl ester to which polyglycine was added as catalyst. Determinations of the amine nitrogen by the van Slyke method indicated an increase in reaction rate in these experiments by a factor of 1.5-2.
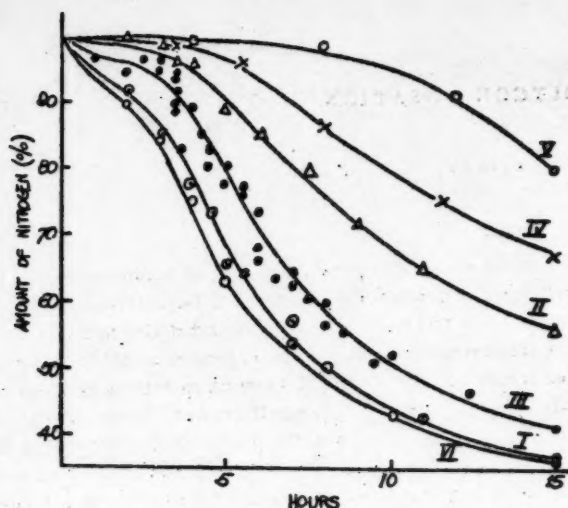
Fig. 1. Dependence of the amount of nitrogen evolved in
the van Slyke determination on the duration of reaction
for the polycondensation of glycine ethyl ester in presence
of 2 mole-% of CO_2: I - 40° with moist ester; II - 30°;
III - 40°; IV - 20°; V - 0°

It was of interest to determine the compositions of the polycondensation products obtained in the period
before the inflection and in the period after it. By use of the method of determining piperazinediones by hy-
drolysis with weak alkalis [4], it was shown that in the first stage of the reaction the content of piperazinediones
in the reaction mixture attains a value of 53%, whereas at the tenth hour of the reaction (at the same tempera-
ture and with the same amount of catalyst) their content is reduced to 11%.

It is interesting that the amount of piperazinedione in the reaction mixture is appreciably dependent on
the temperature at which the experiment is carried out. Fig. 2 gives the results of experiments carried out to
the same progress of reaction, but at different temperatures. These results show quite clearly that rise in
reaction temperature results in an increased yield of piperazinediones in the reaction mixture. This is probably
the explanation of the high yield of piperazinediones obtained from esters of a-amino acids by Fischer's method
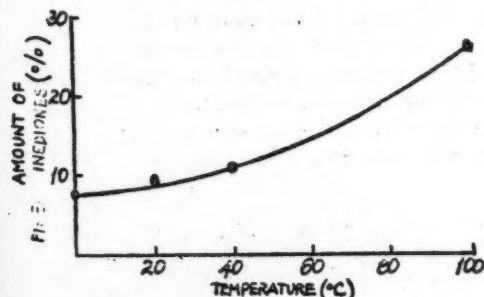[5], in which it is recommended that the esters be heated to a high temperature (about 180°).

Fig. 2. Dependence on reaction temperature of the amount
of piperazinediones found among the polycondensation
products from glycine ethyl ester.

The polycondensation products were
characterized by their solubilities and melting
points.

Particular attention was devoted to the
solubility of the polycondensation products in
water, since this is of great importance in
various chemical and physicochemical inves-
tigations (van Slyke determination of amine
nitrogen, ionophoresis, chromatography, etc.).
The investigations showed that the polyconden-
sation of glycine ethyl ester— which attained
a degree of completeness of 90%— yielded
products that were only partially soluble in
water and gave saturated solutions containing
about 2.5% (on the total weight of the solution)

of polymers and piperazinediones. The remainder of the polycondensate remained insoluble in water, even at
high dilution and when the temperature was raised to 100°. With the object of raising the solubility, we carried

out a series of copolycondensations of glycine ethyl ester with ethyl esters of other α-amino acids: DL-alanine, DL-valine, DL-norleucine, DL-phenylalanine, and L-aspartic acid.

A mixture of esters of definite composition was obtained by the successive selection and weighing of first one component and then the next by the method described previously [1].

The tubes containing the binary mixture of monomers were heated at 40° for 30 hours. The tubes were opened, and their contents were ground to a powder in an agate mortar, washed with absolute ether to remove unchanged monomers and alcohol formed in the reaction, and dried over sulfuric acid in a vacuum desiccator. The properties of the products were then investigated.

The results of these experiments show that, as a rule, these products are more soluble in water than the polycondensation product obtained from a single amino ester. Good results were obtained when the second component was DL-alanine ethyl ester. In illustration of the results we give the graph for the composition-dependence of the melting points and solubilities in water at room temperature of the copolycondensation products from the ethyl esters of glycine and DL-alanine (Fig. 3).

A notable feature is the sharp rise in solubility in water (Curve I) as the composition of the original mixture approaches equimolecular proportions, for which the solubility attains 35%. At this point the aqueous solutions obtained do not contain insoluble particles, such as are present in those obtained from polyglycine, but become completely clear when a slight excess of water is added. It will be seen from the same graph that the melting point of the copolycondensation product also changes as the composition of the original mixture is varied (Curve II), falling to 180° at the point representing equimolecular composition. Melting is accompanied by some darkening in color, but there is no decomposition like that occurring during the melting of poly-DL-alanine (m.p. 240°) and, particularly, polyglycine (m.p. 306°), when complete charring occurs, even in a sealed capillary. It is characteristic that an artificially prepared mixture of polyglycine, poly-DL-alanine, piperazine-dione, and lactimide does not have a sharp melting point, but chars in the range 240-300°. The solubility of such artificial mixtures in water differs little from that of the polycondensation products obtained from pure glycine ethyl ester.
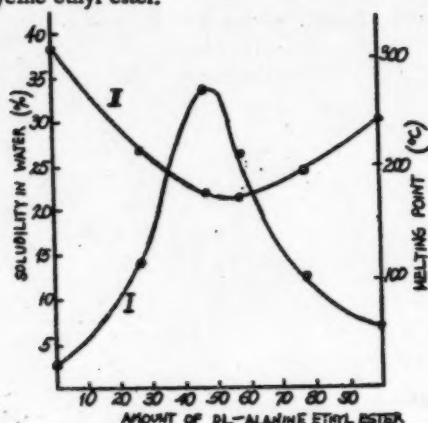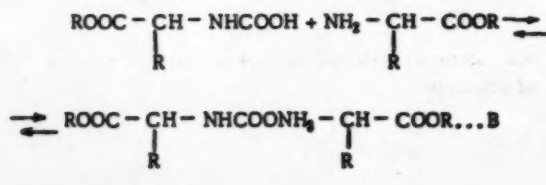

Fig. 3. Dependence of the solubility in water (I) and melting point (II) of a copolycondensation product obtained from the ethyl esters of glycine and DL-alanine on the composition of the original monomer mixture
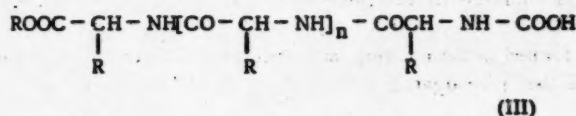
Discussion of Results

It has been emphasized previously [1] that the catalytic action of acidic catalysts is associated with their ability to yield hydrogen ions, which activate the ester linkage in reactions with other substances and with molecules of the same substance. Carbon dioxide is here able to play the part of an acidic substance, in as much as it forms carbamic acid derivatives with esters of α-amino acids:

$$ROOC-\underset{\underset{R}{|}}{CH}-NH_2 \xrightarrow{CO_2} ROOC-\underset{\underset{R}{|}}{CH}-NHCOOH\ldots A$$

$$(I)$$
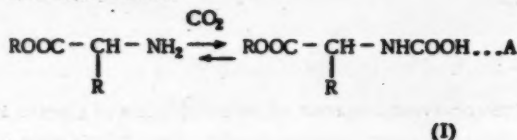
Compounds of the type (I) have been isolated and have been described in the literature [6] as weak unstable acids. The acidic properties of these substances are confirmed by their ability to react with basic compounds, in particular with esters of α-amino acids, to give the corresponding salts (carbamates) (II):

$$ROOC-\underset{\underset{R}{|}}{CH}-NHCOOH + NH_2-\underset{\underset{R}{|}}{CH}-COOR \rightleftarrows$$

$$\rightleftarrows ROOC-\underset{\underset{R}{|}}{CH}-NHCOONH_2-\underset{\underset{R}{|}}{CH}-COOR\ldots B$$

$$(II)$$

The reversibility of the reactions A and B, which has been confirmed by experiment, indicates the complexity of the processes occurring in the reaction mixture yielded by esters of α-amino acids and the probability of the appearance of acidic substances of type (I), able to catalyze the polycondensation of these esters. Moreover, it is possible that carbamic acid derivatives (I) may be formed not only by esters of α-amino acids, but also by their polymers:

$$\text{ROOC} - \underset{\underset{R}{|}}{\text{CH}} - \text{NH[CO} - \underset{\underset{R}{|}}{\text{CH}} - \text{NH]}_n - \text{COCH} - \text{NH} - \text{COOH}$$

$$\underset{R}{|}$$

(III)

The compounds (III) will clearly have acidic properties and will be able to yield free hydrogen ions, which will activate the ester linkages of neighboring molecules.

It is highly probable that a definite time will be required for the formation of the compounds (III); accordingly, in the initial period (up to three hours) the reaction rate is lower than in the subsequent period (after three hours).

As regards the catalytic effect of moisture on the reaction studied, it must be remembered that water readily hydrolyses ester groupings — both those of the esters of α-amino acids, and also those of the polymers [7] to carboxyl groups. The latter — as shown by the effect of the addition of polyglycine as catalyst— have the usual catalytic effect. It is characteristic that the α-amino acids themselves have no catalytic action on the reaction of the glycine ester.

As regards the increased solubilities and lower melting points of the copolycondensation products formed by glycine ethyl ester with esters of other α-amino acids, these results are in accord with the variations in properties observed in other copolymers [9].

With regard to the increase in the proportion of the piperazinedione component of the reaction mixture as the reaction temperature is raised, this phenomenon may result not only by direct cyclization of dipeptides, but also by thermal degradation of the polymers to dimers followed by cyclization to piperazinedione [10]. Experiments in which polyglycine was subjected to prolonged heating at 100° showed that there was an appreciable increase in the proportion of piperazinedione in products obtained by the polycondensation of glycine ethyl ester at room temperature.

SUMMARY

1. An investigation was made of the kinetics of the polycondensation of glycine ethyl ester in presence of carbon dioxide as catalyst. It was shown that both moisture and also polyglycine itself had catalytic effects on this reaction.

2. It was shown that, as the reaction temperature was raised, there was an increase in the content of cyclization products in the mixture obtained by the polycondensation of glycine ethyl ester.

3. The copolycondensation of the ethyl esters of glycine and DL-alanine was investigated, and the properties (solubility in water, melting point) of the products were studied.

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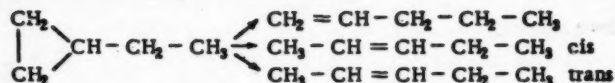
BRIEF COMMUNICATIONS

ISOMERIZATION OF ETHYLCYCLOPROPANE ON SILICA GEL UNDER THE
CONDITIONS OF CHROMATOGRAPHIC ADSORPTION ANALYSIS

B.A. Kazansky, V.T. Aleksanyan, M. Yu. Lukina,

A.I. Malyshev, and Kh. E. Sterin

In the preparation of highly pure saturated hydrocarbons it is usual, as a preliminary to distillation through efficient columns, to remove possible impurities by chromatographic adsorption on silica gel. However, experiment shows that silica gel is not always inert toward the substance receiving chromatographic treatment, and it may sometimes act as an isomerizing agent. For example, in an investigation of the behavior of certain terpenes in presence of silica gel under the conditions generally met in the chromatographic separation of mixtures, Arbuzov and Isaeva [1] found that dipentene, pinene, and 3-carene underwent partial isomerization. Among the isomerization products from dipentene they found terpinolene and p-cymene; pinene was partially converted into camphene, dipentene, and terpinolene; and 3-carene was isomerized into dipentene and terpinolene. Dipentene evidently isomerizes by displacement of the double bond, whereas pinene and 3-carene isomerize at the expense of the bridge linkages taking part in three- and four-membered rings. Boord and coworkers [2] found that 1,1,2-trimethylcyclopropane was isomerized in presence of silica gel at room temperature, but the authors did not identify the reaction products. These various observations indicated that it would be of interest to investigate the behavior of monocyclic hydrocarbons of the cyclobutane and cyclopropane series in presence of silica gel, a matter that has not yet been the subject of special study.

We observed recently [3] that isopropylcyclobutane can be filtered through silica gel without undergoing isomerization, and therefore can be purified by this method. When we attempted to purify ethylcyclopropane synthesized by reduction of the hydrazone of cyclopropyl methyl ketone — it was found that unsaturated compounds made their appearance in the hydrocarbon after its contact with silica gel. In order to investigate this phenomenon, we filtered ethylcyclopropane — which had been distilled through an efficient column and, judging by its constants, was very pure — through a layer of silica gel. Investigation of the product with the aid of Raman spectra showed that it contained 2-pentene (in the form of cis and trans isomers) and 1-pentene. Hence, under the influence of contact with silica gel, ethylcyclopropane is partially isomerized into these alkenes:

$$
\begin{array}{c}
CH_2 \\
| \quad \diagdown \\
\quad \quad CH - CH_2 - CH_3 \\
| \quad \diagup \\
CH_2
\end{array}
\rightleftarrows
\begin{array}{l}
CH_2 = CH - CH_2 - CH_2 - CH_3 \\
CH_3 - CH = CH - CH_2 - CH_3 \quad cis \\
CH_3 - CH = CH - CH_2 - CH_3 \quad trans
\end{array}
$$

These results are in accord with the above-mentioned observations on the isomerization of 3-carene, and they permit us to conclude that silica gel is not a suitable sorbent for the chromatographic purification of substances containing a cyclopropane ring.

EXPERIMENTAL

The ethylcyclopropane taken (10.4 g) had b.p. 36.0° (760 mm), n_D^{20} 1.3786; d_4^{20} 0.6840, and aniline point + 17.9° (the literature [4] gives 35.94° (760 mm), n_D^{20} 1.3786; and d_4^{20} 0.6839); it was filtered through a column containing 160 g of silica gel (type: KSM, (a) 14.7). The temperature of the water cooling the silica gel was + 1.7°. The duration of the experiment was ten hours. The product (8.84 g) distilled over at 34.0-36.5° (731.5 mm) and had n_D^{20} 1.3792; and d_4^{20} 0.6740; it immediately decolorized bromine water.

Below, we give the Raman spectrum of the product.

$\Delta \nu$ (cm^{-1}; the intensities are given on a 10-point scale): 309 (0.b), 351 (0), 372 (3.b), 410 (2.b), 443 (5.b), 460 (0), 487 (4), 580 (0.b), 624 (0), 707 (0), 725 (1), 749 (7), 766 (1.doublet), 789 (0), 800 (1.b), 813 (5.b), 860 (4), 890 (5.b), 919 (8.sh), 940 (0), 955 (0), 970 (0), 987 (0), 1017 (2), 1033 (4.b), 1064 (2), 1088 (4), 1109 (3), 1129 (0), 1172 (2), 1200 (10), 1243 (2.b), 1266 (2.b), 1289 (3), 1310 (4), 1332 (1.b), 1381 (5), 1428 (3), 1444 (9.b), 1645 (1), 1659 (6.sh), 1675 (8.sh).

For the quantitative determination of the composition of the mixture obtained, we used the spectrum of 1-pentene, which we have determined previously [5], the spectrum of ethylcyclopropane*, and the spectra of the stereoisomeric 2-pentenes. Since the spectra given in the literature for the 2-pentenes were obtained by the photoelectric method, we made an approximate recalculation of the intensities to the cyclohexane scale used in our measurements; the relative error in the determination of the content of 2-pentenes may therefore be somewhat higher than the errors for ethylcyclopropane and 1-pentene.

On the basis of the spectrum results we determined the composition of the mixture to be as follows: ethylcyclopropane 68%, cis-2-pentene 12%, trans-2-pentene 17%, and 1-pentene 3%.

SUMMARY

1. It was found that, when ethylcyclopropane was filtered through a layer of silica gel (the relative weights of hydrocarbon and silica gel being: 1 : 16), 32% of it underwent isomerization.

2. It was shown that the product of the isomerization of ethylcyclopropane consisted mainly of cis- and trans-2-pentenes.

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DEPENDENCE OF THE KINETICS OF THE DECOMPOSITION OF CYCLOHEXENE ON THE STRUCTURE OF THE CATALYST

E.K. Mankash and V.V. Shchekin

In the estimation of catalytic activity, the importance of Kinetic methods that take account not only of the chemical composition of the catalyst, but also of its physical structure, is being increasingly recognized. The treatment of kinetics in association with the structure of catalysts, and therefore with due consideration of diffusion phenomena, was developed by Zeldovich [1] as early as 1939. The theoretical work of Zeldovich [1], and also of Thiele [2], found its continuation in the work of Wheeler [3], Wagner [4], Hougen and Watson [5], Boreskov [6], and others.

In order to verify the part played by diffusion in its dependence on catalyst structure, we made use of the results of experiments on the transformations of cyclohexene over a series of aluminosilicate catalysts of identical composition but different structures, the temperature being 316° and the space velocity 1 liter/liter·hour. The amount transformed was taken to be the sum of saturated hydrocarbons and polymers calculated as percent by weight on the original raw material. In all cases, since the particle radii of the catalysts did not exceed 100 A, we shall assume Knudsen diffusion [3, 7].

In order to calculate the accessibility of the catalyst surface under the conditions of the reaction studied, we used Wheeler's equation [3], which was derived for the case of heterogeneous unimolecular gas reactions in a stream:

$$hthh = \frac{a^2}{18D_k} \frac{F}{C_A} \frac{1}{\rho v} \ln\frac{1}{1-y} \quad (1)$$

$$\frac{1}{h} thh = f, \quad (2)$$

in which f is the accessibility, as a fraction of unity,

  h is a dimensionless parameter,
  a is the grain diameter of the catalyst (cm),
  D_k is the Knudsen diffusion coefficient (cm²/sec),
  C_A is the reactant concentration (mole/cc),
  ρ is the density of the catalyst substance (account being taken of the porosity) (g/cc),
  v is the specific volume of pores (cc/g),
  y is the fraction of the substance transformed,
  F is the rate at which the reactant is supplied (moles per cc of catalyst per second).

In an inactive catalyst the reactant molecules may penetrate deeply into the pores before reacting, whereas, when the catalyst is an active one, reaction starts immediately near the entrances of the pores. Hence, the accessibility of the surface is greater for an inactive catalyst than for an active one, and the intrinsic activity of a catalyst, taking the effect of structure into account, is characterized by a rate constant for the given reaction of k_s, which is given by the equation:

$$-\frac{dn}{dt} = k_s C_A^n ds, \quad (3)$$

in which $\frac{dn}{dt}$ is the number of moles in each cc reacting per second at a surface of area ds in contact with reactant at concentration C_A, and n is the order of the reaction.

The temperature-dependence of k_s is in accord with the Arrhenius equation, and, when account is taken of the accessibility, a knowledge of it enables the activation energy to be determined.

Equation 1 can be written:

$$hthh = r k_v,$$ (4)

in which $k_v = \frac{F}{C_A} \ln \frac{1}{1-y}$ is a first-order rate constant referred to unit volume of catalyst (seconds); it depends on the properties of the reactant. The value of $\underline{z} = \frac{a^2}{18 D_k \rho v}$ is a constant for a given catalyst at a given temperature, and it is determined by the catalyst structure. The parameter $\underline{h}$ is determined by the ratio of the kinetic and diffusion constants:

$$h = \frac{L}{\sqrt{r}} \sqrt{\frac{k_s}{D_k}},$$ (5)

in which L and $\underline{r}$ are respectively, the length and radius of the pores (cm).

For high values of $\underline{h}$ (h 2), the value of $\underline{f}$ approximates to $\frac{1}{h}$. The parameter $\underline{h}$ can be regarded as a diffusion-retardation factor, directly proportional to the length of the pores and inversely proportional to their size. When the limiting effect of diffusion is increased, the accessibility of the surface $\underline{f}$ diminishes. If, taking Equation 1 into account, we replace $hthh$ in Equation 4 by its equivalent $\underline{h}^2 f$, we obtain the relationship between k_v and the accessibility and retardation coefficients $\underline{f}$ and $\underline{h}$:

$$k_v z = h^2 f$$ (6)

It can be seen from Equation 1 that, for constant temperature and a given reaction, $hthh$ is directly proportional to a^2 and inversely proportional to D_k and $\underline{v}$. When $D_k v < 3 \cdot 10^{-3}$, the value of $\underline{f}$ rapidly falls and so becomes more and more important. When $D_k v > 3 \cdot 10^{-3}$, the accessibility of the surface is already more than 95%, the part played by diffusion factors rapidly diminishes, and the reaction passes into the kinetic region. Equation 1 and the conclusions derived from it are applicable only in a definite range of values of $h > 0.3$, when $\underline{h}$ is proportional to $\sqrt{\frac{ls}{D_k}}$, i.e. under kinetic conditions complicated by diffusion. At very high values of $\underline{h}$, reaction goes only at the surface, and the process assumes a purely diffusional character. The intrinsic rate constant for the reaction k_s may be found from the equation

$$k_s = \frac{9 h^2 f D_k}{a^2}.$$ (7)

Substituting the value of h^2 from Equation 7 into Equation 6 we obtain

$$k_v z = f \frac{k_s a^2}{D_k 9 r},$$ (8)

whence

$$\frac{k_v}{f} = k_s \frac{2v}{r} \rho = k_s s_0 \rho$$ (9)

or

$$k_v = k_s s_{eff} \rho = k_0 s_0 \rho.$$ (10)

in which $k_0 = \frac{k_v \cdot W}{S}$; s_0 is the specific surface of the catalyst (sq-cm/g); $s_{eff} = s_0 f$; $\rho = \frac{g}{W}$ (g is the weight, and W the volume of the catalyst).

It should be noted that Equation 1 does not take account of retardation of reaction by chemical causes (e.g. by reaction products, etc.); it provides kinetic relationships determined only by the structure of the catalyst in the region of kinetics complicated by diffusion.

TABLE 1

Structural Characteristics of Catalysts

Catalyst No.	sq·cm/g	cm	cc/g	cm^2/sec	vD_k 10^3
1	665	9.0	0.300	2.35	0.71
2	715	10.0	0.358	2.61	0.93
3	704	10.0	0.352	2.61	0.92
4	667	10.4	0.347	2.71	0.94
5	422	25.1	0.527	6.55	3.45
6	404	47.3	0.953	12.35	11.75
7	308	74.0	1.123	19.32	21.73

TABLE 2

Kinetic Characteristics of Catalysts

Catalyst No.	y	k_v	h	hthh	f	$s_{eff} \cdot 10^{-4}$ (sq·cm/g)	$\sqrt{\dfrac{1s}{D_k}}$ x10^5	k_s 10^3	k_0 10^3
1	0.840	0.242	1.49	1.34	0.60	400	6.66	10.50	6.3
2	0.800	0.213	1.15	0.94	0.715	512	5.45	7.78	5.6
3	0.733	0.174	1.02	0.77	0.77	542	4.85	6.12	4.8
4	0.767	0.192	1.05	0.82	0.75	497	5.0	6.76	5.1
5	0.603	0.125	0.40	0.14	0.95	399	3.0	5.96	5.7
6	0.493	0.09	0.108	0.031	0.99	400			
7	0.233	0.035	0.04	0.007	1.00	308			

As can be seen from Tables 1 and 2, Experiments 6 and 7 were carried out in the kinetic region with complete accessibility to catalyst.

SUMMARY

1. With the transformation of cyclohexene over aluminosilicate catalysts varying in structure taken as example, it has been shown that the kinetic method of assessing catalyst activity from rate constants that take retardation by diffusion into account (k_s) is applicable to such transformations.

2. It was shown that the value of the dimensionless parameter $\underline{h}$ is a characteristic of the extent of diffusional retardation, being proportional to the ratio of kinetic and diffusion rates.

3. It was shown that the value of the reaction rate constant k_0 does not depend on the surface area.

4. Wheeler's equation was transformed into a simple form of relationship between the constants k_v, k_0, and k_s and the value of the effective (accessible) surface, i.e. the physical properties of the catalyst.

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SYNTHESIS AND PROPERTIES OF (1-CYANO-1-METHYLETHOXY) SILANES

A.D. Petrov, V.F. Mironov, and V.M. Vdovin

Organosilicon compounds in which 1-cyano-1-methylethoxy groups are attached to the silicon atom are of interest on account of the stability of this group to hydrolysis [1]. The properties of these compounds are similar to those of compounds containing highly branched aliphatic radicals attached to a silicon atom, not only through oxygen, but also through NH and sulfur [2]. However, unlike the latter compounds, (1-cyano-1-methylethoxy) silanes, and methods for their synthesis, have as yet received very little study.

Compounds of this type were first prepared from chloromethylsilanes and acetone cyanohydrin (2-methyllactonitrile) by Frisch and Wolf [1], who also established their stability to hydrolysis and noted the absence of any odor of hydrocyanic acid.

However, Hahn [3], who also synthesized similar compounds from silicon tetrachloride and the cyanohydrins of acetone and other ketones, states that the hydrolysis of these compounds is accompanied by an odor of hydrocyanic acid. In the present investigation we have prepared some new (1-cyano-1-methylethoxy) silanes by reaction in accordance with Scheme 1 between acetone cyanohydrin and alkyl-or aryl-chlorosilanes, and we find that these substances do not eliminate hydrogen cyanide in the course of hydrolysis or during storage.

$$1. \; R_nSiCl_{4-n} + (4-n-m) \; HOC(CH_3)_2CN \xrightarrow{\text{pyridine}}$$

$$\rightarrow R_nSiCl_m[OC(CH_3)_2CN]_{4-n-m},$$
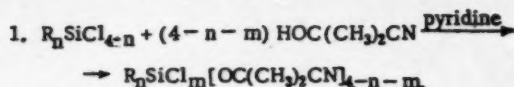
in which $R = CH_3$, C_2H_5, C_6H_5, H, CH_2Cl, $CHCl_2$; $n = 0-3$; $m = 0-2$.

It is noteworthy that $[NCC(CH_3)_2O]_4Si$ is very readily formed from silicon tetrachloride and acetone cyanohydrin (55.6% yield), whereas the syntheses of $(tert-C_4H_9O)_4Si$ and $(tert-C_4H_9NH)_4Si$ require very severe reaction conditions [4, 6]. In this reaction, apart from (1-cyano-1-methylethoxy) silanes, we obtained 3-5% of higher-boiling compounds, the analyses and molecular refractions of which indicate them to be the corresponding disiloxanes, formed as a result of the hydrolysis of Si—Cl bonds, probably by water eliminated from acetone cyanohydrin.

EXPERIMENTAL

We describe the syntheses of the two compounds $R_2Si[OC(CH_3)_2CN]_2$ and $RCl_2Si[OC(CH_3)_2CN]$. The rest of the compounds listed in the table were synthesized in an analogous manner; the relative amounts of reactants and conditions of synthesis were the same for Compound 9 (see table) as for Compound 3.

Dichloro (1-cyano-1-methylethoxy) ethylsilane ($C_2H_5)Cl_2Si[OC(CH_3)_2CN]$). Acetone cyanohydrin (59 g, i.e. 0·7 mole) was added over a period of three hours to a cooled stirred mixture of 342 g (2.1 moles) of $C_2H_5SiCl_3$, 56 g of pyridine, and 500 ml of benzene. After one day pyridine hydrochloride was filtered off and washed with two 100-ml portions of benzene. Benzene and $C_2H_5SiCl_3$ were distilled off, and vacuum distillation of the residue yielded four fractions:

Fraction I, B.p. 30 – 76° (8mm); 24 g
Fraction II, B.p. 77 – 80° (9mm); 84 g
Fraction III, B.p. 89 – 138° (15mm); 5 g
Fraction IV, B.p. 138 – 143° (15mm); 11 g

Fractions II and IV were found to be Compounds 6 and 7, respectively (see table).

TABLE

No.	Formula of substance	Yield (%)	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Molecular refraction [5]		Analysis for Si (%)	
						Found	Calculated	Found	Calculated
1	$(CH_3)HSi[OC(CH_3)_2CN]_2$	72.2	108(14mm)	1.4130	0.9644	54.90	54.97	13.20; 13.16	13.21
2	$(C_2H_5)_2Si[OC(CH_3)_2CN]_2$	60.3	141-2 (19mm)	1.4270	0.9576	68.20	68.36	10.62; 10.98	11.03
3	$(C_6H_5)CH_3Si[OC(CH_3)_2CN]_2$	81	153-4 (4mm)	1.4780	1.0327	79.05	79.16	9.91; 9.83	9.77
4	$(ClH_2C)CH_3Si[OC(CH_3)_2CN]_2$	77.5	114 (3mm)	1.4380	1.0702	63.94	64.18	10.38; 10.01	10.75
5	$(Cl_2HC)CH_3Si[OC(CH_3)_2CN]_2$	40.8	139 (3mm)	1.4462	1.1374	69.22	69.11	13.39; 13.61	13.28
6	$(C_2H_5)Cl_2Si[OC(CH_3)_2CN]$	55.6	78 (9mm)	1.4288	1.1211	48.76	48.58	10.77; 10.72	10.76
7	$(C_2H_5)ClSi[OC(CH_3)_2CN]_2$	11.8	139-140 (15mm)	1.4320	0.9735	–	63.48	10.87; 10.75	10.78
8	$(C_6H_5)Cl_2Si[OC(CH_3)_2CN]$	82.2	116 (2mm)	1.4995	1.1915	64.41	63.89	7.28; 7.44	7.68
9	•$[NCC(CH_3)_2O]_4Si$	55.8 m.p. • 92-94° C without recrystallization							

• The literature [3] gives m.p. 96°, yield 3.6%.

Bis(1-cyano 1-methylethoxy)methylphenylsilane

$(CH_3)C_6H_5Si[OC(CH_3)_2CN]_2$. To a cooled stirred mixture of 80 g (1 mole) of pyridine, 85 g (1 mole) of acetone cyanohydrin, and 150 ml of benzene, 96 g (0.5 mole) of $CH_3(C_6H_5)SiCl_2$ was added over a period of 30 minutes. After one day the precipitate formed was filtered off and washed with benzene. Vacuum distillation yielded four fractions:

Fraction I, B.p. 20-149° (4 mm); 17 g
Fraction II, B.p. 149-156° (4 mm); 115 g
Fraction III, B.p. 155-200° (4 mm); 2 g
Fraction IV, B.p. 200-203° (3 mm); 3.5 g

Fraction II was found to be Compound 3 (see table). Fraction IV had n_D^{20} 1.4800 and d_4^{20} 1.0645, and was probably $[CH_3C_6H_5(NC-\overset{CH_3}{\underset{CH_3}{C}}-O)Si]_2O$; found MR 113.30, calulated MR 117.52.

Found %: Si 13.09, 13.22
$C_{12}H_{22}N_2Si_2O_3$. Calculated%: Si 12.67

Similar fractions were obtained in the synthesis of Compound 2, b.p. 153-154° (5 mm); n_D^{20} 1.4332; d_4^{20} 0.9734;

Found MR 95.23 for $[(C_2H_5)_2(NC-\overset{CH_3}{\underset{CH_3}{C}}-O)Si]_2O$; calculated 95.42.

Found %: C 53.86; 53.80
H 8.85; 8.92
Si 14.80; 14.58
$C_{16}H_{32}N_2Si_2O_3$. Calculated%: C 53.89
H 9.04
Si 15.71

In the synthesis of Compound 5 we obtained a substance having b.p. 176-178° (1 mm); n_D^{20} 1.4563; d_4^{20} 1.2052; found MR 98.91; calculated 97.22; it was probably

$$\left[(CCl_2HC)CH_3 \left(\overset{CH_3}{\underset{CH_3}{NC-C-O}} \right) Si \right]_2 O$$
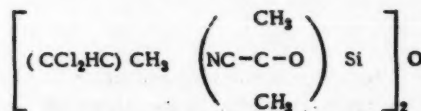
SUMMARY

1. A study was made of the reactions of acetone cyanohydrin with chlorosilanes containing methyl, ethyl, phenyl, chloromethyl, and dichloromethyl substituents, and including also silicon tetrachloride.

2. It was found that steric hindrance was absent in the synthesis of $\left[\overset{CH_3}{\underset{CH_3}{NC-C-O}} \right]_4 Si$
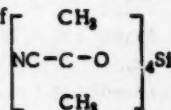
from silicon tetrachloride and acetone cyanohydrin.

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ORGANOBORON COMPOUNDS

COMMUNICATION 4. SYNTHESIS OF DIALKYLBORINIC ESTERS WITH THE AID OF LITHIUM REAGENTS

B.M. Mikhailov and T.A. Shchegoleva

Several methods are known for the synthesis of dialkylborinic esters, but they are all of limited application. For example, diethylborinic esters can be prepared by the action of aldehydes on triethylborine [1], and butyl dibutylborinate has been prepared by the oxidation of tributylborine with moist air [2]. These methods have not been extended to the preparation of other borinic esters. A more general method is that based on reaction between an alkyl magnesium halide and butyl ethylene borate [3], by means of which ethylene bis(dibutylborinate) and ethylene bis(diisopentylborinate) have been prepared in 45-47% yield. However, like the previous methods, this method does not enable us to prepare borinic esters in which two different hydrocarbon radicals are attached to boron.

A promising method for the synthesis of esters of this last type is one based on the use of organolithium compounds. One of us, in collaboration with Aronovich, found [4] that organolithium compounds react smoothly with areneboronic esters with formation of diaryl— and alkylaryl-borinic esters. In the further development of this synthesis of organoboron compounds we found that dialkylborinic esters can be synthesized in good yield by the action of alkyllithiums on alkaneboronic esters. This method enables us to prepare not only those borinic esters in which the alkyl radicals on the boron are identical, but also the previously inaccessible esters in which the alkyl radicals are different.

The present paper describes the preparation of the butyl esters of dibutyl - and butylpropyl-borinic acids by the action of butyllithium and propyllithium, respectively, on dibutyl 1-butaneboronate:

$$\text{n-C}_4\text{H}_9\text{B(O n-C}_4\text{H}_9)_2 + \text{RLi} \rightarrow \begin{array}{c} \text{n-C}_4\text{H}_9 \\ \diagdown \\ \text{B} - \text{O} - \text{n-C}_4\text{H}_9 \\ \diagup \\ \text{R} \end{array}$$

$$\text{R} = \text{n-C}_4\text{H}_9; \quad \text{n-C}_3\text{H}_7$$
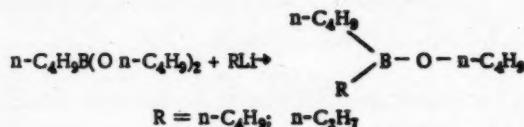
EXPERIMENTAL*

Butyl Dibutylborinate. Over a period of one hour at $-70°$, a solution of 53 g (0.25 mole) of dibutyl 1-butaneboronate in 50 ml of ether was added to a stirred solution of butyllithium, prepared at $0°$ from 43 g (0.31 mole) of butyl bromide and 4.17 g (0.6 mole) of lithium in 225 ml of ether. The reaction mixture was stirred for a further four hours at the same temperature and was then set aside overnight. On the next day dry hydrogen chloride was passed until the reaction mixture was saturated, the ether was distilled off, and the precipitate of lithium halides was filtered off. The precipitate was washed with benzene, and solvent and butyl alcohol were vacuum-distilled from the filtrate and washings; precipitate that formed was again filtered off. The resulting liquid was distilled through a 20-cm column. The product was 36.5 g (74.5%) of butyl dibutylborinate, b.p. 122-124° (33 mm) and d_4^{20} 0.8077.

Found %: B 5.62

$C_{12}H_{27}BO$. Calculated %: B 5.46

The reported boiling point of butyl dibutylborinate is 120-121° (24 mm) [2].

Butyl Butylpropylborinate. Reaction between 0.25 mole of dibutyl 1-butaneboronate and 0.25 mole of propyllithium was carried out under the conditions described above. The product was 25.4 g (57%) of butyl butylpropylborinate, b.p. 84-86° (10 mm), d_4^{20} 0.7888.

* All operations were carried out in an atmosphere of nitrogen.

Found %: C 71.47; H 13.75; B 5.91

$C_{11}H_{25}BO$. Calculated %: C 71.75; H 13.68; B 5.88

SUMMARY

Treatment of alkaneboronic esters with alkyllithiums yields dialkylborinic esters.

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* T.p. = C.B. Translation pagination.

CURRENT EVENTS

GENERAL MEETING OF THE DIVISION OF CHEMICAL SCIENCES OF THE U S S R
ACADEMY OF SCIENCES ON THE PEACEFUL USES OF ATOMIC ENERGY *

On July 2-5, 1955, after the plenary session of a general meeting of the Academy of Sciences of the USSR devoted to a discussion of the peaceful uses of atomic energy, there was a session of the Division of Chemical Sciences of the Academy of Sciences at which chemical aspects of the same subject were discussed. The meetings of the session were held in the large auditorium of the Chemistry Department of the M.V. Lomonosov State University, Moscow, and they were well attended by Soviet scientists.

The following foreign guests took part in the work of the session: Prof. T. Padenrecht and Prof. T. Sikeland**from Norway; Prof. S. Claesson from Sweden; Prof. E. Leibnitz from the German Democratic Republic; Prof. J.H. de Boer from Holland; Prof. J. Maly from Czechoslovakia; Prof. D. Grdenic and Prof. P. Savic from Yugoslavia; Prof. D. Shankar from India; Prof. E. Schmidt and Prof. B. Karlik from Austria; and Prof. Horna Holubei**from Rumania. When opening the first meeting of the session, the chairman, Academician M.M. Dubinin, presented the foreign guests, who were warmly welcomed by the participants.

The first day of the session was devoted to problems in radiation chemistry. V.L. Karpov, Cand. Chem. Sci., read a paper entitled "Action of Nuclear Radiations on High Polymers" (the paper was written conjointly with Academician V.A. Kargin, and B.N. Zvereva, I.Ya. Petrova, and N.A. Slovokhotova also participated in the work). The speaker pointed out that the problem studied is of interest in connection with the use of plastics, rubbers, etc. in presence of high-energy radiation. He pointed out also that the irradiated material might undergo desirable changes of properties under such conditions— for example, change into an infusible, insoluble condition ("radiational vulcanization"), into a state of chemical unsaturation, or into a form of lower molecular weight. The study of such processes may be of interest also for the understanding of the action of ionizing radiations on biological systems, such as proteins, polypeptides, etc.

The results of the investigations show that three main types of processes are to be observed in presence of nuclear radiations: degradation, cross linking of molecular chains, and far-reaching decomposition with formation of gaseous products, the relative extents to which these processes occur being mainly dependent on the chemical nature of the polymer and its molecular structure. The type and energy of the radiation play a very much smaller part: α-particles, fast electrons, and γ-rays produce qualitatively identical changes in a polymer of a given type.

N.A. Bakh, Doctor Chem. Sci., read a paper entitled "Action of Ionizing Radiations on Aqueous Solutions of Inorganic Salts". The speaker remarked that it is not yet fully clear what oxidation and reduction reactions occur in aqueous solutions of inorganic salts under the action of ionizing radiations and in what way these reactions are interrelated. As a result of the interaction of the primary products of the radiolysis of water among themselves and with the original components of the system— cations, anions, and dissolved gases - new components appear, and these, in their turn, take part in reactions— both radiation-induced reactions, and also in thermal reactions. The radiation-induced reactions occurring in aqueous solutions of iron salts, potassium iodide, and sodium nitrate were examined. The irradiation was carried out in glass apparatus designed in various ways, so that the reactions occurring in the systems could be investigated both during the irradiation and after irradiation had ceased. In the main, X-rays of about 90 kv hardness were used, and the dosages ranged up to 2000 roentgens per second. A study was made of the dependence of the observed effects on concentration,

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* The papers read at this conference are available in Consultants Bureau English Translation.
** Spelling of these names rendered phonetically from Russian.

pH of the solution, and the identities of the dissolved gases (present at saturation concentration) for various overall doses.

A paper entitled "Sensitization and Suppression of Oxidation-Reduction Reactions Occurring During Radiolysis" was read by M.A. Proskurnin, Cand. Chem. Sci., who wrote the paper in collaboration with V.D. Orekhov and E.V. Barelko. The speaker stated that, in the utilization of the energy of nuclear radiation for bringing about chemical processes, it is very important to determine the yields of the radiation-induced reactions that will occur under the given conditions. He maintained that, without a clear understanding of the mechanisms of the processes leading to the sensitization of desirable reactions and the suppression of undesirable reactions, we cannot hope for success in the development of radiation-induced processes.

In a paper entitled "Regularities Observed in the Mechanism and Kinetics of Simple Radiation-induced Reactions (Formation of Ozone and Oxidation of Nitrogen)", S. Ya. Pshezhetsky pointed out that it is important to determine the distinguishing features of radiation-induced reactions, considered in their relation to thermal and photochemical reactions, and to establish their specific laws. The speaker presented some data for two reactions in which simple molecules take part: the formation of ozone and the oxidation of nitrogen, the radiation used being γ-rays from Co^{60}, 200-300-kev electrons, and electrons having an energy of a few hundred electron-volts. Both reactions were studied in the gas and liquid phases, and in both cases charge-transfer processes occur in collisions of ions with atoms and molecules, excited species undergo deactivation processes, and the recombination of atoms and other reactions occur in the reaction space and at the walls. The results presented by this speaker indicate the probable direct participation of ions in radiation-induced reactions — they may, in fact, play a very important part.

On the second day, the session of the Division of Chemical Sciences, with Academician A.P. Vinogradov in the chair, considered matters relating to the action of high-energy particles on atomic nuclei.

A paper on nuclear fission reactions due to negative pions and fast protons was read by N.A. Perfilov, Doctor Phys. Math. Sci., whose co-authors were N.S. Ivanova, O.V. Lozhkin, V.I. Ostroumov, and V.P. Shamov.

The interaction of slow negative pions with nuclei from the end of the periodic system was investigated by the method of thick-layer photographic plates. Experiments were carried out on U, Bi, and W nuclei, which have differences in charge of 9 and 18 units. Nuclear fission reactions due to 160-Mev and 660-Mev protons were also studied by the same method.

The numerous experiments carried out by the authors have enabled them to extend the existing concepts of the mechanism of fission processes and have shown that excitation energy does not pass into the kinetic energy of the fission fragments. An analysis of uranium fissions shows that the nucleus undergoing fission emits approximately as many charged particles (and therefore as many neutrons) as it would be expected to emit on the assumption that the whole of the excitation energy is removed by evaporation of neutrons and charged particles. The authors consider, however, that the agreement found between the experimental and calculated values is not an indisputable proof of purely emissional fission, since different variants of the theory of evaporation may give somewhat different values for the number of charged particles. An analysis of bismuth fissions shows that, as a result of the preliminary "cooling" process, the excited nucleus emits neutrons and charged particles in such numbers that the fission parameter Z^2/A rises to the value at which the fission value is lowered to the binding energy of the neutrons of the residual nucleus. A similar analysis for tungsten showed that fission occurs from a level somewhat above the level for emissional fission, but, as in the cases of uranium and bismuth, after preliminary cooling with emission of a considerable number of neutral and charged particles. The speaker remarked that, in order to create a complete theory of fission, it is essential that further investigation be made into the details of fission processes.

V.I. Baranov, Doctor Phys. Math. Sci., whose co-authors were Academician A.P. Vinogradov, I.P. Alimarin, Corr. Memb. Acad. Sci. USSR, A.K. Lavrukhina, T.V. Baranova, F.I. Pavlotskaya, A.A. Bragina, and Yu. V. Yakovlev, reported on a radiochemical investigation of the fission of bismuth, thorium, and uranium with 480-Mev protons The main object of the investigation was the determination of the laws relating the yield distributions of the various fission products to the identity and energy of the bombarding particle, and also the discovery of new isotopes obtained by bombardment with high-energy protons. The investigation enabled the authors to present a general picture of the nuclear processes occurring. Formation of light nuclei, fission processes, and spallation processes were observed. It was shown that the yield distribution of the fragments with respect to mass number is symmetrical and has a single broad maximum, and it was pointed out that the characteristic features of the fission processes of uranium and thorium resulting from the action of particles of

various energies are identical. These peculiarities are also features of the fission processes of other heavy elements. It was stated that the fission of bismuth is preceded by the emission of, on the average, 2 protons and 16 neutrons, a fact that indicates that emmisional fission occurs.

V.N. Mekhedov, Cand. Chem. Sci., whose co-authors were B.V. Kurchatov, M. Ya. Kuznetsova, and L.N. Kurchatova, described a radiochemical investigation of the fission of tungsten with 280-Mev deuterons. A sample of tungsten trioxide was specially purified for the experiments, and this was irradiated in the deuteron beam for one hour. After the irradiation the various radioactive isotopes were separated out on suitable carriers. Altogether, 28 radioactive isotopes – mainly in the range $Z = 33$-52 were isolated and studied. In addition, calcium, nickel, antimony, and cesium were isolated, but the low activities of the samples did not permit reliable identification of the isotopes formed.

Energy considerations indicated that for 280-Mev deuterons an evaporation mechanism cannot result in the formation of the isotopes found, which differed from tungsten by 40 or more units of mass. It must be considered, therefore, that the products obtained resulted from the fission of tungsten nuclei. The formation cross section for individual isotopes in the region of the yield maximum was found to be about 10^{-28} sq. cm, which is not in conflict with the total fission cross section of tungsten ($\sigma = 1.1 \cdot 10^{-27}$ sq. cm).

B.V. Ershler, Doctor Chem. Sci. (co-authors: G.M. Kukavadze, M.P. Anikina, and L.L. Goldin), discussed the yields of various neodymium and cerium isotopes in the fission of uranium-233. A sample of U^{233} was irradiated for a long time in a nuclear reactor, after which it was set aside for six months and then dissolved, together with its platinum envelope, in aqua regia. The rare earths were separated on an yttrium carrier and subjected to mass-spectrometric analysis. The yields (%) were: $Ce^{140} - (5.6 \pm 0.17)$; $Ce^{142} - (5.6 \pm 0.17)$; $Nd^{143} - (5.15 \pm 0.3)$; $Nd^{144} - (3.37 \pm 0.3)$; $Nd^{145} - (3.00 \pm 0.2)$; $Nd^{146} - (2.34 \pm 0.15)$; $Nd^{148} - (1.15 \pm 0.10)$; $Nd^{150} - (0.51 \pm 0.04)$%.

A.K. Lavrukhina, Cand. Chem. Sci. (co-authors: Academician A.P. Vinogradov, I.P. Alimarin, Corr. Memb. Acad. Sci. USSR, V.I. Baranov, T.V. Baranova, and F.I. Pavlotskaya) described a radiochemical investigation of the spallation of copper and bismuth nuclei with high-energy particles. The object of the investigation was the determination of the main peculiarities of the spallation process in light and heavy nuclei and the effect of the kind and energy of the bombarding particles on the character of the process. From the character of the spectra of the radioactive nuclei formed, it was possible to show that a great variety of nuclear processes, occur when copper and bismuth are bombarded with 480-Mev protons, namely, emission of light nuclei, nuclear fission and spallation, and secondary reactions leading to the formation of nuclei of atomic number higher than that of the original nucleus. The application of the method of extrapolation and interpolation to the determination of the yields of short-lived and stable nuclei enabled the authors to obtain a complete picture of the yields of spallation products obtained from copper irradiated with 680-Mev protons, to determine the total cross section for the spallation process, to establish the position of the region of nuclei obtained in maximum yield, and to estimate the proportion of stable isotopes in the spallation products of copper.

A.N. Murin, Doctor Chem. Sci., who collaborated with B.K. Preobrazhensky, I.A. Yutlandov, and M.A. Yakimov, read a paper on the spallation and fission reactions of complex nuclei (Cu, La, Bi) bombarded with 480-Mev and 660-Mev protons. Targets of the chemically pure elements or their oxides were used, and these were irradiated with protons in the internal beam of the synchrocyclotron of the Institute of Nuclear Problems of the USSR Academy of Sciences. The reaction products were isolated on inert carriers by the usual methods. The authors established that in all cases the main bulk of the reaction products were formed by a spallation process, i.e. by cascade ejection of nucleons from the target nucleus and subsequent evaporation of protons, neutrons, and α-particles. In the process of evaporation from the excited nuclei, neutrons predominate over charged particles.

The determination of the yields of spallation products enabled the authors to make an approximate estimate of the average excitation energy of the intermediate nuclei, which are formed as a result of a nuclear-cascade process and which emit nucleons and α-particles by evaporation. In this way the mean excitation energy for bismuth was found to be of the order of 90 Mev. The speaker stated that reaction products that are comparatively distantly removed with respect to Z and A from the irradiated nucleus (such as calcium in the irradiation of copper) are probably formed by a mechanism differing from that of the formation of nuclei that are not far-removed from the target nucleus. The yields of Co^{56} from Cu^{63} $[Cu^{63}(p; 3p, 5n) Co^{56}]$ and Co^{58} from Cu^{65} $[Cu^{65}(p; 3p, 5n) Co^{58}]$and also of Mn^{54} from Cu^{65} and Mn^{52} from Cu^{63} are very close in value,

whereas the yields of Ca^{47} [Cu^{65} (p; 4α, 2p, n) Ca^{47}] and Ca^{46} [Cu^{63} (p; 4α, 2p, n) Ca^{46}] differ very greatly. The radioactive isotopes Ce^{134} (T = 2.2 days) and Cs^{128} (T = 2.5 minutes) were first detected in these experiments.

B.V. Kurchatov, Cand. Chem. Sci., whose co-authors were V.N. Mekhedov, N.I. Borisova, M. Ya. Kuznetsova, L.N. Kurchatova, and L.V. Chistyakov, gave a paper entitled "Radiochemical Investigation of the Products of the Spallation of Silver with High-energy Particles", which described the results of a study of the nuclear reactions occurring when silver is irradiated with 550-Mev α-particles, 280-Mev deuterons, and 480-Mev protons. The metallic silver used in this work was extremely pure. About 70 products of the spallation of silver were detected, and the following previously unknown isotopes were estimated and investigated: Cd^{104}, Cd^{10}, Ag^{103}, Mo^{90}, Sr^{83}, Sr^{82}, Rb^{82}.

The last day of the session, which was under the chairmanship of Academician I.I. Chernyaev, was devoted to the application of isotopes in chemical investigations.

A.I. Brodsky, Corr. Memb. Acad. Sci. USSR, devoted his review paper to the investigation of the structures and reactivities of compounds with the aid of isotopes. He emphasized that the study of isotopic exchange provides direct information on the mobilities of atoms in molecules and the dependence of mobility on structure, and it enables us to make a closer approach than can be made by any other method to the solution of a problem that is of the greatest importance for theoretical chemistry — the relationship of reactivity and reaction mechanisms to chemical structure. The speaker referred to the suggestion he made in 1949 to the effect that the peculiar features of exchange at different X–H bonds are associated with the state of the electron shell of the reaction center – in this case the atom X. A.I. Brodsky later developed these ideas in greater detail and confirmed them experimentally. When the atom X has a free (unshared) pair of electrons, deuterium becomes attached by this pair and a proton is simultaneously released from another pair. Exchange of this type is immeasurably fast, irrespective of the structural peculiarities of the molecules, the protolytic properties of the medium, and the presence of catalysts. When there is no free pair on the atom X, the deuteron can become attached only by the pair that was originally binding the proton. This process, unlike the previous one, requires a comparatively high activation energy, and exchange occurs only under favorable conditions, created either by the effect of substituents on the electron density around the atom X and on the strength of the bond X–H, or by strongly acid or basic donors or catalysts. It is generally considered that such exchange proceeds via electrolytic dissociation; an example is found in hydrogen exchange at C–H bonds in various organic compounds. The results of investigations discussed by the speaker enabled him to conclude with reasonable certainty that tautomerism is absent in H_3PO_3, phosphites, and hypophosphites, but present in H_3PO_2, which is as yet the only proved example of tautomerism in inorganic compounds. With the aid of radioactive sulfur it was confirmed that, as suggested by A.E. Arbuzov, the rearrangement of diethyl sulfite into ethyl ethanesulfonate is irreversible.

In a discussion of hydrogen mobility and hydrogen exchange in organic compounds, the speaker examined possible reaction mechanisms: ionization and electrophilic mechanisms, and also exchange by the formation of a nucleophilic fourfold complex with displacement of electrons to hydrogen (deuterium) or with intermolecular transfer of hydride ions.

The speaker cited also the results of investigations by A.N. Nesmeyanov and coworkers, and also by other workers, on the effect of σ-π-conjugation and the mutual orientation of bonds on the reactivity of hydrogen in organic compounds.

A.I. Brodsky discussed also the dependence of oxygen exchange on molecular structure, the mechanism of halogen exchange, the structure of complex inorganic molecules, and other topics.

A.A. Grinberg, Corr. Memb. Acad. Sci. USSR, devoted his review paper to the investigation of the structures and reactions of complex compounds by the method of labeled atoms. He stated the most important of the conclusions that can be drawn from the results of the investigation of these matters by Soviet and foreign workers. He pointed out that the stability of complex compounds (characterized by the value of the instability constant) by no means always determines the rate at which exchange occurs. For example, the bivalent platinum compounds studied, though the most stable in the sense of secondary dissociation, were the most labile from the point of view of kinetics. Further investigations carried out by the speaker and his coworkers showed that the relationship between the exchange rate and the nature of the anion, as found for bivalent platinum compounds, can be extended, in the main, to quadrivalent platinum compounds. The speaker

described recent experiments on the rate of isotopic exchange in palladium systems in which exchange was so rapid that the kinetics could not be studied by the usual methods. On the other hand, in an iridium system at concentrations of the order of $10^{-3} - 10^{-2}$ molar, exchange was almost absent. The speaker discussed recent experiments by Ya. A. Fialkov and coworkers on the exchange of SO_4^{2-} between the outer and inner spheres in green chromisulfate complexes, and also the work of V.I. Spitsyn and coworkers on iso- and hetero-poly acids.

G.P. Miklukhin, Doctor. Chem. Sci., discussed the mobility of sulfur in sulfur-carbon bonds and the mechanism of the action of rubber-vulcanization accelerators. He concluded that, in the majority of cases, the compounds having the most mobile sulfur atoms are at the same time also the most effective accelerators for the vulcanization of rubber. Thus, in presence of potassium ethylxanthate the vulcanization of rubber proceeds at room temperature, dithiocarbamates are accelerators for vulcanization under mild conditions, Captax is a typical accelerator for hot vulcanization, and so on. The speaker emphasized the great importance of the investigation of the exchange reactions of sulfur in organic compounds for the elucidation of a number of problems in sulfur chemistry and, in particular, for the establishment of the mutual effects of atoms and the effect of σ,π-conjugation on the mobility and reactivity of sulfur in various compounds.

A closely related theme was treated by E.N. Guryanova, Cand. Chem. Sci., who read a paper entitled "Sulfur Exchange in Polysulfides and in Various Vulcanization Accelerators" (co-authors: V.N. Vasilyeva and L.S. Kuzina).

V.I. Kuznetsov, Doctor Chem. Sci., discussed the use of organic coprecipitants in analytical chemistry. He stated that organic coprecipitants, like the inorganic agents, are able to precipitate micro quantities of elements quantitatively from extremely dilute solutions of the latter — for example, 10^{-6} g of the element from a volume of several liters. Organic coprecipitants, however, have certain characteristic features: they can be removed from precipitates by simple ignition, they are almost devoid of any tendency to adsorb inorganic ions, they are highly specific in action, their range is almost unlimited, and so on.

The speaker examined the coprecipitation of elements in the form of normal salts, in the form of complex and internal-complex compounds formed by the action of organic reagents, and under some other conditions.

V.I. Kuznetsov emphasized that the study of the theory and the development of the application of organic coprecipitants are impossible without the use of radioactive tracers. He pointed out that this new group of organic reagents will be useful for the purpose of improving the methods of separating and purifying radioactive tracers.

The last speaker of the session was S.T. Konobeevsky, Corr. Memb. Acad. Sci. USSR, who discussed the phase diagrams of some plutonium systems. He referred to methods that he had developed for the preparation of homogeneous alloys and for the metallographic, X-ray, thermal, and dilatometric study of metallic plutonium and its alloys on samples weighing from ten micrograms to tens or hundreds of milligrams. With the aid of these methods the phase diagrams of systems formed by plutonium with various metals were studied, and these studies enabled the speaker to establish certain regular features in the properties of alloys formed by plutonium with other elements.

Among those joining in the discussions on the papers were A.M. Zhirmunsky, Corr. Memb. Acad. Sci. White-Russian SSR, I.A. Kazarnovsky, Corr. Memb. Acad. Sci. USSR, Prof. P.I. Dolin, Prof. B.A. Dogadkin, S.Z. Roginsky, Corr. Memb. Acad. Sci. USSR, Academician A.N. Frumkin, V.I. Spitsyn, Corr. Memb. Acad. Sci. USSR, I.P. Alimarin, Corr. Memb. Acad. Sci. USSR, and Academician A.P. Vinogradov.

In a concluding address, Academician M.M. Dubinin surveyed the achievements of the three-day session in the three main sections of the program and drew attention to certain features of this conference. He pointed out that several very important problems of chemistry had been treated for the first time in lectures and discussions at a session of the Division of Chemical Sciences. It is regrettable, said M.M. Dubinin, that the limited time allotted to the program did not permit the inclusion of all of the papers submitted, and in this connection it might be added that a case could be made out for the systematic inclusion of papers on the use of atomic energy — both in purely chemical investigations, and also in technological processes — at sessions of the Division of Chemical Sciences.

Academician M.M. Dubinin referred to the interest taken in the proceedings of the session by the foreign guests, who had systematically attended all of the meetings. Soviet scientists — said M.M. Dubinin were glad to share the results of their investigations on the peaceful use of atomic energy and would welcome the further development of scientific contact between Soviet and foreign workers in all of the fields covered by the Division of Chemical Sciences. The most effective way in which such contacts can be made is by reciprocal visits to scientific institutes and by participation in joint scientific meetings. In conclusion, Academician M.M. Dubinin said that the interest taken by the Soviet chemical community in the meetings of this session was most graphically shown by the overflowing auditorium and the great activity of the participants.

After drawing attention to the substantial scientific achievements of the session of the Division of Chemical Sciences of the Academy of Sciences of the USSR on the peaceful uses of atomic energy, Academician M.M. Dubinin thanked all the speakers for the great trouble they had taken in the preparation of their papers and he thanked also the numerous participants of the session, who by their questions and discussions had helped to make it a success.

All the papers read at the session of the Division of Chemical Sciences of the USSR Academy of Sciences are included in the collected papers, published in Moscow (1955) under the title "Conference of the Academy of Sciences of the USSR on the Peaceful Uses of Atomic Energy, June 1-5, 1955".